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(54) POLYMER COMPOSITE, MICROEMULSION AND THEIR PREPARATION

(57)Abstract:

PURPOSE: To provide a polymer composite which has a bicontinuous structure of two substantially nonporous phases and is prepd. by the aq. photopolymn. of a hydrophilic monomer and a hydrophobic monomer in the presence of a surfactant and a lipophilic photoinitiator in a microemulsion comprising an aq. phase and an oil phase.

CONSTITUTION: (A) 2-40 wt.% water, (B) 2-60 wt.% ethylenically unsatd. polar monomer such as an oil-insoluble free-radically (co)polymerizable polar monomer, an oil-insoluble or water-and oil-soluble free-radically (co)polymerizable polar monomer, a water-and oil-soluble free-radically (co)polymerizable monomer, or their mixture, (C) 15-85 wt.% free-radically polymerizable ethylenically unsatd. hydrophobic monomer, (D) 5-70 wt.% surfactant such as a nonionic, cationic, or anionic surfactant or their mixture which does not copolymerize with ingredients B and C or an unsatd. nonionic, cationic, or anionic surfactant or their mixture which copolymerizes with ingredients B and C, and (E) 0.01-5 wt.% lipophilic photoinitiator are compounded and photopolymerized, giving the objective polymer composite.

JAPANESE

[JP,07-224105,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART TECHNICAL PROBLEM
MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS CORRECTION OR
AMENDMENT

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]it is the polymer composite which has a nonporous double continuation structure substantially, including an optical start polymerization product of microemulsion which has aqueous phase and an oil phase, — said microemulsion — the following — (a) — the (e):(a) water 2 – 40 weight %;

(b) following the (1) – (4) and (1) — the radical polymerization nature of oil insolubility substantially, or copolymeric polar monomer;

(2) Radical polymerization nature or copolymeric polar oligomer of oil insolubility or water solubility, and oil solubility;

(3) Water-soluble and oil-soluble radical polymerization nature or a copolymeric monomer;

(4) A mixture of these;

2 to 60 weight % of radical copolymeric ethylene system unsaturation polarity kinds chosen from a ***** group;

(c) 15 to 85 weight % of radical copolymeric ethylene system unsaturation hydrophobic monomers;

(d). Do not carry out copolymerization to a polar kind of (1) ingredient (b), and a monomer of an ingredient (c). A nonionic surface active agent, a cationic surface active agent, anionic surface active agents, and these mixtures, (2). Copolymerization can be carried out to a polar kind of an ingredient (b), and a monomer of an ingredient (c). An ethylene system unsaturation nonionic surface active agent, a cationic surface active agent, anionic surface active agents and these mixtures, the surface-active agent 5 chosen from a group which comprises both (3), (1), and (2) – 70 weight %; and the (e) oleophilic photoinitiator 0.01 – five weight sections; [However, weight % of the above (a), (b), (c), and (d). The amount of photoinitiators of (e) on the basis of gross weight of microemulsion, respectively The above (a), Said polymer composite in which it includes that it is based on gross weight of (b), (c), and (d)], and said optical start polymerization product has a nonporous double continuation structure substantially.

[Claim 2]Following (a) – (c) : (a) and (1) water;

(2) An ethylene system unsaturation polar monomer or oligomer of at least one sort of radical polymerization nature;

(3) Accept necessity and it is a water-soluble radical photopolymerization initiator.;

(4) Accept necessity and it is a water-soluble radical thermal polymerization initiator.;

(5) Accept necessity and it is a water-soluble additive.;

(6) Aqueous phase which contains auxiliary solvent; refractoriness polarity oligomer; and if needed [(7)] if needed;

(b) A radical polymerization nature ethylene system unsaturated monomer of (1) hydrophobicity;

(2) Polymerization nature or a copolymeric polar kind;

(3) An oleophilic radical photopolymerization initiator;

(4) Accept necessity and it is an oleophilic radical thermal polymerization initiator.;

(5) Accept necessity and it is a cross linking agent.;

(6) Accept necessity and it is a chain transfer agent;

(7) Microemulsion containing oil phase; and (c) surface-active agent; which contain oil-soluble additive agent; refractoriness polarity oligomer; and if needed [(8)] if needed.

[Claim 3]The polymer composite according to claim 1 in which said microemulsion contains further a water-soluble radical photopolymerization initiator of 0.1 - 1 weight section to gross weight of the ingredient 1 (b), 1 (c), and 1 (d), or the microemulsion according to claim 2.

[Claim 4]Said microemulsion A water-soluble cross linking agent, a pH adjuster, an electrolyte, Polymer composite of Claim 1 or 3 descriptions which contain further a color, paints, a compound [activity / in drugs], and a water-soluble additive agent chosen from a group which comprises an activity compound, an auxiliary solvent, non-copolymeric polarity oligomer, and these mixtures physiologically, Claim 2, or microemulsion given in three.

[Claim 5]Following steps (a) - (c) : (a) and (1) water;

(2) An ethylene system unsaturation polar monomer or oligomer of at least one sort of radical polymerization nature;

(3) Accept necessity and it is a radical photopolymerization initiator;

(4) Accept necessity and it is a radical thermal polymerization initiator;

(5) Accept necessity and it is a water-soluble additive.;

(6) Accept auxiliary solvent; and (7) necessities if needed, and it is refractoriness polarity oligomer.;

A process of preparing the first mixture of ***** in an inert atmosphere;

(b) and (1) — at least 1 sort of hydrophobic radical polymerization nature ethylene system unsaturated monomer;

(2) A radical photopolymerization initiator;

(3) Accept necessity and it is a radical thermal polymerization initiator.;

(4) Accept necessity and it is a cross linking agent.;

(5) Accept chain transfer agent; and (6) necessities if needed, and it is refractoriness polarity oligomer.;

A process of mixing said first mixture into said second mixture in existence of a surface-active agent, and forming microemulsion under process; which prepares the second mixture of *****, and the (c) inert atmosphere while stirring quietly;

A manufacturing method of ***** microemulsion.

[Claim 6](a) process; which manufactures microemulsion by a method of a description to Claim 5, and (b) — a manufacturing method of polymer composite which has a nonporous double continuation structure substantially containing process; which irradiates said microemulsion with a radiant ray and forms polymer composite.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the polymer material which has a nonporous double continuation structure substantially. A nonporous double continuation (bicontinuous) structure is the structure where both of hydrophilic polymer phases and hydrophobic polymer phases are continuing, and each phase moreover shows each bulk properties, substantially. This invention relates also to the manufacturing method of the microemulsion to which a radical polymerization nature monomer exists in both the aqueous phase and an oil phase, and such microemulsion, and the method of reaching and manufacturing a polymer material.

[0002]

[Description of the Prior Art] A surfactant mixture with suitable microemulsion They are water / oil system colloidal dispersion object stable with [a surface-active agent usually like soap and an auxiliary surface-active agent (cosurfactant) like short chain alcohol]. In contrast with the turbidity emulsion of custom in which stability originates in kinetics purely, microemulsion is thermodynamically stable and is spontaneously formed by contact. It is one with a small (about 10 nm) size of the globular form droplet currently distributed in a continuation medium, and is optically transparent. Encyclopedia of Polymer Science Engineering; Wiley: Please refer to New York 1987 Vol. 9 and p.718.

[0003] Microemulsion differs from a macro emulsion or a mini emulsion. It is an unstable mixture thermodynamically, and one liquid forms the fine droplet for which the bigger diameter containing two sorts of immiscible liquids than 100 nm is shown, and is distributing the macro emulsion usually known as an emulsion in the liquid of another side. The macro emulsion has become muddy and is usually carrying out opalescence. A mini emulsion is an opaque thermodynamically unstable emulsion containing two sorts of immiscible liquids prepared using the mixture containing the auxiliary surface-active agent and ionic surfactant like long chain fatty alcohol or n-alkane. In order to prepare a mini emulsion with an average droplet diameter of 100-500 nm, comparatively high mechanical shearing force is required.

[0004] Microemulsion can be an oil-in-water type (water continuation type), a water-in-oil type (oil continuation type), or double continuation type. In double continuation microemulsion, an oil phase and the aqueous phase live together as a continuation domain, and surfactant molecules are located in the interface. The water in a double continuation microemulsion system, an oil, and an auxiliary surface-active agent (usually short chain alcohol) are diffused at the speed which is equal to the speed for Sumishige, respectively.

[0005] The radical polymerization of a vinyl monomer can be attained in either the disperse phase of an oil-in-water type (o/w), a water-in-oil type (w/o), or double continuation microemulsion, or a continuous phase in principle. Kuo and others (Macromolecules, 1987, 20, p.1216) has indicated polymerizing styrene in the disperse phase of o/w type microemulsion. Candau and others

(US,4,681,912,B Description) has indicated polymerizing water soluble monomers in the disperse phase of w/o type microemulsion. Chew and Gan (J. Polym. Sci.: Polym. Chem., 1985, 23, p.2225) tended to polymerize the methyl methacrylate as a continuous phase of a w/o type emulsion which distributed water in the polymer matrix. However, proof that the obtained polymer has taken double continuation structure is not accepted at all. Stoffer and Bone (J. Dispersion Sci. Technol., 1980, 1, p.37). It has reported having polymerized the methyl methacrylate as a continuous phase in the system which contains sodium dodecyl sulfonate, a pentanol, and water further.

[0006]Shah and others (European patent application No. 391,343) has indicated polymerizing for example, the acrylate system monomer as a disperse phase of aqueous microemulsion, and manufacturing a very small polymer particle. Puig and others (J. Colloid Interface Sci., 1990, Vol. 137, p.308) is discussing the polymerization of the acrylic acid / styrene system microemulsion of a monomer which shows [in / on the other hand (acrylic acid) / the aqueous phase] fusibility remarkably. The obtained copolymer has constituted the form which an acrylic acid unit is dispersed and is distributed at random in a polystyrene block object.

[0007]Above-mentioned document is only teaching the thermal method of making a polymerization starting. There is nothing that has indicated manufacturing the double continuation polymer with which the polymer which has the double continuation structure where both phases are solids or a hydrophobic polymer, and hydrophilic polymer coexist in both phases in these document by the polymerization of microemulsion moreover.

[0008]Price (US,5,151,217,B Description), It has indicated manufacturing the double continuation microemulsion containing the hydrophobic monomer and cross linking agent like alkyl ester of styrene, acrylate, or methacrylate under existence of a unique addition condensation nature cationic surface active agent. The purpose of Price was to manufacture the solid polymer which can be used for a separation process with photopolymerization method. About using a polar monomer for the method of polymerizing the microemulsion which makes a radical polymerization nature monomer exist in both the aqueous phase and an oil phase, a manufacturing method, or one of phases, it is unstated in any way. Finally, output polymer is not two solid phases and shows one solid phase and one liquid phase.

[0009]There is a report by Cheung and others about photopolymerization of double continuation microemulsion (Langmuir, 1991, Vol. 7, pp. 1378ff., and 2586ff.). Porosity polystyrene membrane is obtained from the microemulsion of styrene/drainage system. It polymerizes in the case where methyl methacrylate / acrylic acid series microemulsion is not considered as the case where a surface-active agent is made to exist, and it is supposed that the porous polymer solid which has good mechanical stability in both cases was obtained. According to the report, although the polar monomer is used by these systems, the obtained copolymerization material shows the single phase porosity system by the microscopic inspection.

[0010]European patent publication of unexamined application 0th transferred to the grantee of this invention 432 According to the No. 517 gazette, forming a porous film, film, or bead is indicated by carrying out photopolymerization of the canal phase of the double continuation microemulsion which contains an activity substance further biologically. However, about the polymerization of the monomer in a hydrophilic phase, neither a description nor claim for patent is carried out at all.

[0011]The US,5,238,992,B Description (Outubuddin) has indicated the composite material and microemulsion polymer blend which were manufactured from the microemulsion containing both a hydrophilic phase and a canal phase and which controlled porosity. This microemulsion contains a surfactant system, an arbitrary auxiliary solvent, and a hydrophilic monomer in a hydrophilic phase, and is prepared as a thing which contains a hydrophobic monomer in a canal phase. As for the obtained blend, even if a stoma is shown in both a micron field and a submicron region and being compared with any of an oil-in-water type or a water-in-oil type, when microemulsion is double continuation type, it is common that porosity becomes high.

[0012]

[Problem to be solved by the invention]In the technical field concerned, neither the polymer which has a nonporous double continuation structure substantially also being manufactured, nor the needs for such polymer are recognized. These polymer that has a nonporous double continuation structure substantially, The hydrophilic polarity kind of the radical polymerization nature contained in the aqueous (water) phase of microemulsion and the hydrophobic monomer of the radical polymerization nature contained in an organic (oil) phase are polymerized simultaneously, and it is obtained by forming the polymer which has two sorts of solids which have a nonporous double continuous phase substantially.

[0013]Such polymer that has a nonporous double continuation structure substantially has the useful bulk properties of both hydrophilic polymer and a hydrophobic polymer for especially the use searched for. For example, to moisture and/or bacteria, while it is impermeableness, a breathable film with the high transportability of a steam is desired dramatically. In such polymer, either a hydrophobic substance or a hydrophilic substance can be caught or released gradually. The material in which another bulk properties of one side of a phase or both have an advantage demonstrated simultaneously can also be manufactured. For example, the adhesive acrylate type adhesives made into conductivity can be manufactured by making a hydrophilic phase contain an electrolyte.

[0014]This invention provides the formation method of the microemulsion in which a solid contains both the manufacturing method of a nonporous double continuation polymer material and such a material, and a hydrophilic radical polymerization nature polarity kind and a hydrophobic radical polymerization nature monomer substantially, and such microemulsion.

[0015]

[Means for solving problem]The polymer composite of this invention includes the optical start polymerization product of the microemulsion which has a nonporous double continuation structure substantially and has the aqueous phase and an oil phase. said microemulsion — the following — (a) — the (e);(a) water 2 [about] — about 40 weight %;

(b) the radical copolymeric ethylene system unsaturation polarity kind 2 [about] — about 60 weight %;

(c) the radical copolymeric ethylene system unsaturation hydrophobic monomer 15 [about] — about 85 weight %;

(d). Do not carry out copolymerization to the polar kind of (1) ingredient (b), and the monomer of an ingredient (c). A nonionic surface active agent, a cationic surface active agent, anionic surface active agents, and these mixtures, (2). Copolymerization can be carried out to the polar kind of an ingredient (b), and the monomer of an ingredient (c). An ethylene system unsaturation nonionic surface active agent, a cationic surface active agent, anionic surface active agents and these mixtures, the surface-active agent 5 [about] chosen from the group which comprises both (3), (1), and (2) — about 70 weight %; and the (e) oleophilic photoinitiator 0.01 [about] — about 5 weight sections; It includes [however, the amount of photoinitiators of (e) is based on the gross weight of the above (a), (b), (c), and (d) for weight % of the above (a), (b), (c), and (d) on the basis of the gross weight of microemulsion, respectively]. Said both of polymerization products have a double phase of the double continuation structure which is a nonporous solid substantially.

[0016]The unique double continuation polymer system of this invention is acquired as a result of carrying out the simultaneous polymerization of the radical pile affinity kind in both the aqueous phase of microemulsion, and an organic phase. At the time of the simultaneous polymerization in each phase, the aqueous phase and an organic phase live together in the state of the mutually united continuation domain. They are double continuity.

[0017]In this way, while the polymerization in the aqueous phase brings about the hydrophilic polymer which has hydrophilic bulk properties, the polymerization in an oil phase brings about the hydrophobic polymer which has hydrophobic bulk properties. Since a simultaneous polymerization takes place, the polymer composite of nonporosity substantially which has both hydrophilic polymer and a hydrophobic polymer is obtained. There is that no one of polymer serves as a disperse phase

substantially, it lives together as a domain where both of the polymer continued substantially, and the composite material obtained as a result serves as nonporosity and double continuity substantially. This polymer composite has two solid phases, and one hydrophilic polymer and the hydrophobic polymer of another side live together as a nonporous double continuation structure substantially.

[0018]Although not limited to a specific theory, the polymer composite of this invention has both a hydrophobic continuous phase and a hydrophilic continuous phase as a form formed when microemulsion is polymerized. A hydrophobic continuous phase is formed when a hydrophobic monomer polymerizes, and a hydrophilic continuous phase is formed when a hydrophilic monomer polymerizes. The microemulsion constituent produced by polymerizing shows the characteristic with both hydrophilic nature which followed the continuous hydrophobicity, and can perform neither of things for which the solvent of a hydrophobic polymer also dissolves the microemulsion constituent produced by the solvent of hydrophilic polymer polymerizing.

[0019]***** [that there are the independent hydrophobic polymer and hydrophilic polymer which are together put at the time of a polymerization so that the mechanical concentration which can resist a solvation may be formed]. About whether copolymerization is carried out, some do not understand the hydrophobic monomer and the hydrophilic monomer at present so that a hydrophobic monomer and a hydrophilic monomer may form concentration of chemical share nature in the field which carried out copolymerization.

[0020]Even if the form of the polymer composite of this invention is a case where an exact form cannot describe with a molecular level, one side of a phase is distributing and another side differs from the two phase form composite material which is continuation. The constituent of this invention is because the bulk properties by the continuity of a hydrophobic polymer phase and the bulk properties by the continuity of a hydrophilic polymer phase are compatible. "Double continuation structure" is a term for describing the form of the microemulsion after the polymerization with which the characteristic by a hydrophobic continuous phase and the characteristic by a hydrophilic continuous phase are compatible.

[0021]The method of this invention is also important for the form of the polymer composite obtained. A mixture remains as microemulsion stable at the time of a polymerization, and in order for the polymer composite moreover obtained to show structure concentration nature, both of the monomers of a kind need to polymerize promptly. The quick and controllable polymerizing method which makes it possible to keep ["freezing" or] the form of microemulsion stable, and to stop the phase separation of microemulsion to the minimum, and to obtain nonporous polymer composite substantially in the case of a polymerization is a radical polymerization method which uses a photoinitiator and an electromagnetism radiant ray. Although it is possible as comparison to form nonporous polymer composite substantially under the heat start radical polymerization conditions using the monomer illustrated by the US,5,238,992,B Description (Outubuddin) under a certain kind of conditions, There is a limitation in the capability for a thermal initiation to be controllable. Since control of polymerization reaction speed is difficult, by the heat induction polymerizing method, there is a possibility that the form of the polymer composite obtained may change. Since this invention tends to control the direction which the form of the microemulsion in the case of a polymerization (microemulsion after the polymerization obtained if it lengthens) depends on the optical starting method compared with the heat starting method and can attain the form of a request of the polymer composite of this invention, photopolymerization method is used for it.

[0022]If the optical start polymerizing method is adopted as an unexpected thing, a nonporous composite material will be formed certainly substantially [request / of this invention]. In order for the Reason which photopolymerization method can trust dramatically to start a polymerization, it is not necessary to change temperature, photopolymerization method stops [that a polymerization is controllable (for example, the case where the electromagnetism radiant ray is irradiated — as long as — a polymerization takes place), and] the phase separation of the microemulsion at the time of

photopolymerization to the minimum — it comes out.

[0023]The US,5,238,992,B Description will have indicated that a porosity polymer blend and a composite material are formed preferentially, if the heat start polymerizing method is used. This invention is not the heat start polymerizing method, and eliminates a porous blend and composite material by providing the polymer composite which was prepared with photopolymerization method and which has a nonporous double continuation structure substantially.

[0024]The term "it is nonporosity substantially" in this Description means that the stoma or open space in a composite material does not exist on the level which exceeds 0.1 micrometer in diameter. "It is nonporosity substantially", The US,5,238,992,B Description and "Preparation and Characterization of Porous Polymers from Microemulsions" (ACS.) of Qutubuddin and others Chapter 5 of Symposium Series384, It is clearly distinguished from the porous structure in the micrometer level indicated to Polymer Association Structures, American Chemical Society, and 1989.

[0025]The aqueous phase is provided with the following.

Water.

At least one sort of radical copolymeric ethylene system unsaturation polarity kinds, for example, a monomer, and/or oligomer.

This aqueous phase if needed A refractoriness polarity oligomer additive agent, a radical polymerization nature photochemistry activation cross linking agent, One or more sorts of ingredients chosen from the group which comprises an auxiliary solvent, a water-soluble radical photopolymerization initiator, a water-soluble radical thermal initiator, and (it is (like the additive agent chosen from the group which comprises an electrolyte, a color, and a substance [activity / in drugs])) a water-soluble functional additive agent can be included further.

[0026]The term "polarity" in this Description means the kind in which a measurable dipole moment is shown, and the term "oligomer" means the polymer kind which has a repeating unit to about 2000 pieces by two or more pieces and the maximum.

[0027]An organic phase contains the ethylene system unsaturation hydrophobic monomer of at least one sort of radical polymerization nature, the ethylene system unsaturation polar monomer of radical polymerization nature, and an oil-soluble radical photopolymerization initiator. The oil-soluble cross linking agent which this organic phase can contribute to the bulk properties of a refractoriness polarity oligomer additive agent and the constituent obtained if needed, One or more sorts of ingredients chosen from the group which comprises an oil-soluble chain transfer agent, an oil-soluble radical thermal initiator, and (as [chose / out of the group which comprises a plasticizer, a color, a substance / activity / in drugs /, and a tackifier]) an oil-soluble functional additive agent can be included further.

[0028]The third basic component of microemulsion is a surface-active agent of nonionic or ionicity (an example, anionic, or cationicity), and compatibility that can be anionic or nonionic preferably. If suitable, it will dissolve in neither an organic phase nor aqueous phase, but an additive agent and a bulking agent (for example, a web, scrim or silica, activity carbon black, or a fibrous filler) by which it is arranged inside the last polymer composite which has a nonporous double continuation structure substantially and in which it deals may be made to contain.

[0029]Even if it mixes an ingredient which composes aqueous phase, an organic phase, and a surface-active agent in which order, transparent microemulsion forms spontaneously. Subsequently, carry out the cast of the microemulsion into a suitable metallic mold, may irradiate with an electromagnetism radiant ray, may carry out a radical polymerization promptly, and. Apply microemulsion on a base material, on the base material, may irradiate with an electromagnetism radiant ray, may carry out a radical polymerization promptly, and, Or the cast of the microemulsion may be carried out so that a sheet or reinforcement of mesh state, for example, scrim etc., may be included, and it may irradiate with an electromagnetism radiant ray, and a radical polymerization may be carried out promptly, in these various methods — "quick" — it means that a polymerization

takes place so that a nonporous double continuation structure may be substantially acquired in polymer composite, without a form of microemulsion changing substantially in the case of a polymerization.

[0030] Preferably, electromagnetism radiant rays are ultraviolet rays which activate a photoinitiator in microemulsion and enable a monomer in microemulsion, and/or a simultaneous polymerization of oligomer. Obtained polymer composite which has a nonporous double continuation structure substantially can be made into adhesiveness and print resistance by operation of a used hydrophobic monomer. This whole system characteristic can be adjusted with an ingredient in both aqueous phase and an organic phase.

[0031] A nonporous double continuation structure can be inspected with a scanning electron microscope substantially [polymer composite / of this invention]. In a micron and a submicron level, as it is in a scanning electron microscope photograph of drawing 4, for example, it turns out that there is not a stoma or open space into polymer composite of this invention.

[0032] The feature of this invention is at a point that the bulk properties of hydrophilic polymer (it polymerizes in aqueous phase of microemulsion) and the bulk properties of a hydrophobic polymer (it polymerizes in an oil phase of microemulsion) live together. Another feature of this invention has a composite material of this invention in improving the conventional hydrophobic polymer with the bulk properties of hydrophilic polymer, and a point which makes the reverse possible.

[0033] The advantage of this invention is that neither of the phases of polymer composite is the disperse phases in which continuity has broken off in the composite material. Another advantage of this invention is that the quick optical start polymerizing method brings about nonporous polymer composite substantially.

[0034] I. Before an aqueous-phase polymerization start, the aqueous phase of microemulsion contains a water-soluble additive agent a water-soluble initiator and if needed water, the ethylene system unsaturation polarity kind of radical (**) polymerization nature, and if needed.

I.a. the microemulsion of Mizumoto invention — the gross weight standard of microemulsion — about 2- about 40 weight % — desirable — about 5- about 30 weight % — and — most — desirable — about 6- about 20weight % of water is included. Preferably, microemulsion contains deionized water.

[0035] I.b. the aqueous phase of ethylene system unsaturation polarity Tanemoto invention of radical (**) polymerization nature — water — in addition, include the ethylene system unsaturation polarity kind of radical polymerization nature. Polar monomers other than the monomer such whose a polar kind is insolubility substantially in an oil phase, and an oil insolubility monomer. It is chosen from (namely, the monomer which are water solubility and oil solubility), and the group which comprises polar oligomer (namely, oligomer which is hydrophilic oligomer or water solubility, and oil solubility which are insolubility substantially in an oil phase). Such a monomer is chosen from the group which comprises polar monomers (namely, water solubility and an oil-soluble monomer) other than the polar monomer which is insolubility substantially, and an oil insolubility monomer in an oil phase.

[0036] microemulsion — the character of a request of polymer composite — the gross weight standard of microemulsion — about 2- about 60 weight % — desirable — about 5- about 50 weight % — and — most — desirable — about 8- about 40weight % of a required polar kind is included cumulatively.

I.b.i. it is insolubility substantially in a polar ethylene system unsaturation radical (**) polymerization nature oligomer oil phase. Or useful polar ethylene system unsaturation radical (**) polymerization nature oligomer which is water solubility and oil solubility, Although not necessarily restricted, polyethylene oxide acrylate, polyethylene oxide diacrylate, What was chosen from the group which comprises polyethylene-glycol acrylate, polyethylene-glycol diacrylate, polyurethane acrylate, polyurethane diacrylate, N-vinyl-pyrrolidone macromere, and those mixtures is included. Polyethylene oxide acrylate and diacrylate are preferred. The most desirable oligomer contains polyethylene oxide acrylate from the Reason of acquisition ease and combination ease. Useful

oligomer for the optimal physical properties (for example, absorptivity, nonporosity nature, intensity) of the polymer composite which usually has a nonporous double continuation structure substantially, about 100 – about 100,000 — desirable — about 100 – about 60,000 — and it has about 100 – about 5000 number average molecular weight most preferably.

[0037]Ib.ii. the polar monomer of the first type of an ethylene system unsaturation polar monomer of the radical (**) polymerization nature of oil insolubility is an ethylene system unsaturation polar monomer of the water-soluble radical (**) polymerization nature which is insolubility substantially in an oil phase substantially. Both "it being oil insolubility (it is insolubility in an oil phase) substantially" and "water solubility." It means that a monomer has less than about 0.5weight % of solubility in an oil phase, and the partition ratio in a predetermined temperature (preferably about 25 ** – 35 **) of the concentration in the oil phase to the concentration in the aqueous phase shows less than about 0.005. Such a monomer may be nonionic, for example, acrylamide, or may be ionicity. The mixture of non-ion and an ionicity monomer may be used. The ionicity monomer which suits these standards, Although not necessarily restricted, sodium styrenesulfonate, acrylic acid potassium, Sodium acrylate, sodium methacrylate, acrylic acid ammonium, Sodium 2-acrylamide 2-methylpropanesulfonate, 4,4,9-trimethyl 4-azonia 7-oxa ***** 9-***** 1-sulfonate, A N,N-dimethyl- N-(beta-metacryloxy ethyl) ammonium propionate betaine, What was chosen from the group which comprises the ethylene system unsaturated monomers of other dipolar ion nature which has trimethylamine methacrylamide, 1,1-dimethyl- 1-(2,3-dihydroxypropyl) amine methacrylamide, and the required requirements for solubility, those mixtures, etc. is included. The desirable polar monomer of oil insolubility from the Reason of the ease of combination, and the physical properties of a request when it polymerizes. What was chosen from the group which comprises acrylamide, sodium styrenesulfonate, sodium acrylate, 2-acrylamido-2-methyl-propane-sulfonic-acid sodium, sodium methacrylate, and those mixtures is included.

[0038]I. Many polar monomers known by this ethylene system unsaturation polar monomer industry of radical (**) polymerization nature other than b.iiiI.b.ii show a certain amount of solubility to both water and an oil. They have about 0.5% or more of solubility in an oil phase, and the partition ratio in a predetermined temperature (preferably about 25 ** – 30 **) of the concentration in the oil phase to the concentration in the aqueous phase shows about 0.005 or more. The radical (**) polymerization nature monomer of the useful polar ethylene system unsaturation which can be distributed between the oil phase of the microemulsion of this invention and the aqueous phase, Although not necessarily restricted, N-vinyl pyrrolidone, N-vinylcaprolactam, (METO) Acrylic acid, hydroxyethyl (METO) acrylate, itaconic acid, What was chosen from the group which comprises styrene-sulfonic-acid, N-substitution acrylamide, N,N-2 substitution acrylamide, N, and N-dimethylaminoethyl methacrylate, 2-acrylamido-2-methyl propane sulfonic acid, and those mixtures is included. The monomer in which desirable polar distribution is possible Acrylic acid (METO), N-vinyl pyrrolidone, What was chosen from the group which comprises N-vinylcaprolactam, N, and N-dimethylaminoethyl methacrylate, N,N-dimethylacrylamide, styrene sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, and those mixtures is included. The monomer in which the most desirable polar distribution is possible from the Reason of desirable character like the physical strength which they can give to polymer composite. What was chosen from the group which comprises acrylic acid, N-vinyl pyrrolidone, N-vinylcaprolactam, N,N-dimethylacrylamide, and those mixtures is included.

[0039]I.c. the water-soluble initiator aqueous phase may contain further the water-soluble radical polymerization initiator chosen from the group which comprises the mixture of a photoinitiator, and a photoinitiator and a thermal initiator if needed.

I.c.i. a water-soluble photoinitiator useful to water-soluble photoinitiator this invention — a radiant ray (usually) When exposed to ultraviolet rays, it is a photoinitiator which generates a free radical, and it acts as an initiator for the polymerization (**) of the following polymerizable surfactant (**), a hydrophilic monomer, an oleophilic monomer, polymerization (**) nature oligomer, and when it exists.

Benzophenone replaced by an ion portion, a hydrophilic portion, or its both although the useful water-soluble photoinitiator was not restricted; An ion portion, The thioxan ton replaced by a hydrophilic portion or its both and 4-substituent contain what was chosen from the group which comprises 4-substitution-(2-hydroxy-2-propyl) phenyl ketone which is ion or a hydrophilic portion. Although such ion or a hydrophilic portion is not necessarily restricted, it contains the portion chosen from the group which comprises hydroxyl, a carboxyl group, and the basis of carboxylate. Although water-soluble useful benzophenone is not necessarily restricted, it contains what was chosen from the group which comprises a 4-trimethyl aminomethyl benzophenone hydrochloride and benzophenone 4-sodium methanesulfonate. Although a water-soluble useful thioxan ton is not necessarily restricted, 3-(2-hydroxy-3-trimethyl aminopropoxy) thioxan ton hydrochloride, What was chosen from the group which comprises 3-(3-trimethyl aminopropoxy) thioxan ton hydrochloride, thioxan ton 3-(2-ethoxysulfonic acid) sodium salt, and thioxan ton 3-(3-propoxysulfonic acid) sodium salt is included. Although water-soluble useful phenyl ketone is not necessarily restricted, ketone (4(2-hydroxy-2-propyl)-diethylene-glycol phenyl), (2-hydroxy-2-propyl) What was chosen from ketone and the group which comprises those water soluble salt is included (phenyl-4-butane carboxylate). A desirable water-soluble photoinitiator is a 4-trimethyl aminomethyl benzophenone hydrochloride.

[0040]the aqueous phase — a standard [weight sections / all the (**) / in microemulsion / heavy affinity kind 100] — about 0.05— about 1 weight section, preferably, the photoinitiator of about 0.1 — about 1 weight section is included, when used.

I.c.ii. a water-soluble thermal initiator useful to water-soluble arbitrary thermal initiator this inventions, When it exists (**) and is exposed [a hydrophilic monomer, an oleophilic monomer, polymerization (**) nature oligomer, and] to the heat which starts the polymerization (**) of a polymerizable surfactant, it is an initiator which generates a free radical, and it indicates in detail to the following. These thermal initiators are used only as assistance of a photoinitiator, when the perfect polymerization of a monomer has concern. Although a water-soluble suitable thermal initiator is not necessarily restricted, potassium persulfate, Ammonium persulfate, sodium persulfate, and those mixtures; A oxidation reduction initiator, For example, resultant; and 4,4'-azobis (the soluble salts 4-cyanopentanone acid and its) of a reducing agent which is chosen from the group which comprises the sodium metabisulfite and sodium bisulfite, and the above-mentioned persulfate What was chosen from the group which comprises (for example, sodium salt and potassium salt) is included. A water-soluble desirable thermal initiator is ammonium persulfate. Preferably, almost all the water-soluble thermal initiator is used at the temperature of about 50 ** — about 70 **, and, on the other hand, a oxidation reduction type initiator is used at the temperature of about 30 ** — about 50 **, the time of being used — a water-soluble thermal initiator — a standard [weight section / in microemulsion / heavy (**) affinity kind 100] — about 0.05— about 0.1 — about 1 weight section are included preferably about 1 weight section.

[0041]I.d. the water-soluble additive agent aqueous phase may contain water-soluble various additive agents further if needed, in order to manufacture the polymer composite which has specific character and/or appearance. Each additive agent is chosen so that a desired final product may be manufactured. For example, supposing a conductive polymer is desired, an electrolyte will be added and it will get. Supposing coloring polymer is desired, a color will be added and it will get. Although the example of a useful additive agent is not necessarily restricted, a water-soluble cross linking agent. What was chosen from (for example, methylenebis acrylamide), a pH adjuster, an electrolyte, a color, paints, the compound [activity / in drugs], and the group that comprises an activity compound, an auxiliary solvent, non-copolymeric polarity oligomer, those mixtures, etc. physiologically is included. Although not necessarily restricted, when it was desirable for polymer composite to be conductivity as for especially the electrolyte containing what chosen from the group which comprises potassium chloride, a lithium chloride, sodium chloride, and those mixtures, the useful thing became clear with various compounds of this invention. On the basis of all the 100

weight sections of the aqueous phase, the electrolyte to about 5 weight sections may be contained at the maximum, and about 0.5 weight sections — about 3 weight sections are contained preferably. [0042] Although non-copolymeric polar oligomer useful as an additive agent is not necessarily restricted, it contains what was chosen from the group which comprises poly(N-vinylpyrrolidone), a polyethylene glycol, poly(oxyethylene) alcohol, poly (ethyleneimine), and those mixtures. Such oligomer is added so that the bulk properties of the obtained polymer composite may be affected, for example, so that hydrophilic nature may be given to this material. The fatty alcohol which has about 1 — a carbon atom of eight abbreviation although the usual auxiliary solvent is not necessarily restricted. (for example, glycerin) and polyether (for example, butyl cellosolve (trademark).) It is butylcarbitol (trademark), hexyl cellosolve (trademark), and hexylcarbitol (trademark), and what was chosen from marketing and the group which comprises those mixtures is altogether included from Union Carbide.

[0043] The thing which is added to the aqueous phase and which show solubility with all the water-soluble organic additive agents specific in the organic phase of microemulsion intrinsically will be understood easily. Each additive agent has the original partition ratio between the aqueous phase and an organic phase. For this reason, as long as there are no directions in particular, the above-mentioned constituent of the aqueous phase exists also in an organic phase, and will affect that character. It is unnecessary to an understanding and implementation of this invention, and to change a fixed quantity of all the specific partition ratios. [the additive agent indicated so far]

II. An oil phase term "organic phase", a "oil phase", and a "lipophilic phase" are used for a mutual compatible target in this Description. Before a polymerization start, the oil phase of microemulsion contains a reactant oleophilic additive agent a hydrophobic radical (**) polymerization nature monomer, a radical (**) polymerization nature polar monomer, an oil-soluble initiator, and if needed. [0044] II.a. in the lipophilic phase of the microemulsion of hydrophobic radical (**) polymerization nature monomer this invention, the useful ethylene system unsaturated monomer of hydrophobic radical polymerization nature, Although not necessarily restricted, what was chosen from the group which comprises the ester derived from about C₁ of acrylic acid or methacrylic acid — abbreviation C₁₈ alkyl ester, i.e., acrylic acid, or methacrylic acid, and about C₁ — abbreviation C₁₈ alcohol is included. Desirable acrylic (METO) acrylate Isononyl acrylate, What was chosen from the group which comprises isooctyl acrylate, 2-ethylhexyl acrylate, ethyl acrylate, n-butyl acrylate, decyl acrylate, dodecylacrylate, isobornyl acrylate, methyl methacrylate, and those mixtures is included. The most desirable alkyl acrylate monomer is chosen from the group which comprises ethyl acrylate, n-butyl acrylate, isooctyl acrylate, isobornyl acrylate, methyl methacrylate, and those mixtures.

[0045] An organic phase contains further the above-mentioned alkyl acrylate monomer and copolymerizable radical polymerization nature ethylene system unsaturation comonomer if needed, in order to change the glass transition temperature (T_g) of the polymer composite obtained. Desirable comonomer Styrene, acrylonitrile, and vinyl ester. Comonomer is chosen by the character of a request of double continuation polymer of the last solid including what was chosen from the group which comprises (for example, vinyl acetate, vinyl propionate, vinyl neo pentanoate, etc.). The double continuation microemulsion of this invention and in order to give the sufficient intensity and cohesiveness for the polymer composite produced by being manufactured, the gross weight standard of microemulsion — about 15— about 85 weight % — desirable — about 25— about 75 weight % — and — most — desirable — about 30— about 65weight % of a hydrophobic monomer is included. The presentation percent of each constituent in microemulsion will be determined by the person skilled in the art on the basis of the character of a request of a copolymer, as stated above. It explains further what selection of the ratio of a constituent is made, and the following embodiments and drawing 1 — the phase diagram of three illustrate it.

[0046] II.b. a radical (**) polymerization nature polar monomer — as mentioned above, in order that an organic substance may distribute between the organic phase/aqueous phase of microemulsion,

the organic phase of microemulsion, Probably, a part of radical polymerization nature polar monomer indicated by above-mentioned I.b.ii. and I.b.iii. is included when used. Each monomer indicated in it shows the original partition ratio, and the listing is not required because of an understanding of this invention, and implementation.

II.c. an oil-soluble initiator oil phase contains an oil-soluble radical photopolymerization initiator (photoinitiator), and contains a thermal initiator further if needed.

[0047]II.c.i. oil-soluble photoinitiator this invention — a useful oil-soluble photoinitiator — a radiant ray (usually) When exposed to ultraviolet rays, a free radical is generated, and it acts as an initiator for the polymerization (**) of a polymerizable surfactant, a hydrophilic monomer and/or oligomer, an oleophilic monomer, and when it exists (**). Although a useful photoinitiator is not necessarily restricted, it is a mixture of one Michler's ketone and benzyl, or benzophenone, What was chosen as 2 US,4,289,844,B which is about 1:4 weight ratio preferably from the photoinitiator system of the coumarin base of a description and the group which comprises preferably the system which uses 3 dimethoxyphenylacetophenone and/or a diethoxyacetophenone as a base is included. An oil-soluble photoinitiator is contained in microemulsion as a part of organic phase at first. The free radical by which it was generated at the time of an exposure performs the polymerization (**) of a monomer, and (**) the polymerization (**) of a polymerizable surfactant by both water and an organic phase. An organic phase contains about 0.01 – the oil-soluble photoinitiator of about 5 weight sections on the basis of all the (**) heavy affinity kind 100 weight section of microemulsion.

[0048]II.c.ii. in manufacture of double continuation polymer of this invention, arbitrary oil-soluble thermal initiator oil-soluble thermal initiators may be used for the above after a photopolymerization process like a description if needed, in order to complete a polymerization reaction. An oil-soluble thermal initiator useful to this invention is an initiator which generates a free radical, when exposed to heat, and it starts a polymerization (**) of a polymerizable surfactant, a hydrophilic monomer, oligomer, an oleophilic monomer, and when it exists, and it explains it to the following in detail. Although a suitable oil-soluble thermal initiator is not necessarily restricted, An azo compound like Vazo 64 (trademark) (2,2'-azobis (isobutyronitrile)) and Vazo 52 (trademark) (2,2'-azobis (2,4-dimethylpentanenitril)) (both are available from duPont); Benzoyl peroxide. And what is chosen from a group which comprises peroxides like lauroyl peroxide and those mixtures is included. A desirable oil-soluble thermal initiator is 2,2'-azobis (isobutyronitrile).

[0049]an organic phase — a standard [weight section / of a polymerization (**) nature compound in microemulsion / gross weight 100] — about 0 – about 5 weight sections — usually — being alike — about 0.05– about 5 weight sections, preferably, about 0.1 – an oil-soluble thermal initiator of about 5 weight sections are included, supposing it is used.

II.d. arbitrary reactant oleophilic additive agent organic phases may contain further one or more sorts of further radical reactivity constituents if needed, and although they are not necessarily restricted, they contain what was chosen from the group which comprises an oil-soluble cross linking agent, chain transfer agents, and those mixtures. Although the example of a useful cross linking agent is not necessarily restricted, divinylbenzene; 1,4-butanediol diacrylate, What was chosen from the group which comprises abbreviation C₄-abbreviation C₈ alkyl diacrylate; which is chosen from the group which comprises 1,6-hexanediol diacrylate, 1, and 8-octanediol diacrylate, and those mixtures is included. A desirable cross linking agent is 1,6-hexanediol diacrylate.

Supposing a cross linking agent is added, it will change, the last physical properties, for example, condensation intensity, of polymer. An organic phase is further included if needed, supposing it uses about 0.1 – the cross linking agent of 75 weight % of abbreviation for about 0 – about 75 weight sections or more than it, and usual on the basis of all the oil phase 100 weight section. The quantity of the cross linking agent used determines the physical properties of polymer, for example, the insolubility to the inside of a solvent, an elastic modulus, and internal strength. In such a use, an organic phase usually contains the cross linking agent of about 5 – about 75 weight sections on the basis of oil phase 100 weight section. In order that a person skilled in the art may acquire desired

physical properties, the quantity of a suitable cross linking agent can be determined, and he will understand that there is no maximum on actual of the cross linking agent by which such a person skilled in the art is used in the compound of this invention and in which it deals.

[0050]An organic phase contains a chain transfer agent further if needed. Although an example of a useful chain transfer agent is not necessarily restricted, it contains what was chosen from a group which comprises carbon tetrabromide, alcohol, mercaptan, and those mixtures. When it exists, a desirable chain transfer agent is isooctylthioglycolate, supposing an oil phase is used — a standard [weight sections / all the / oil phase 100] — the maximum — a chain transfer agent to about 0.5 weight sections — usually — being alike — about 0.01 — a chain transfer agent of about 0.05 — about 0.2 weight sections may be included further preferably about 0.5 weight sections.

I.e. arbitrary refractoriness oleophilic additive agent oil phases contain further one or more sorts of refractoriness oil-soluble additive agents if needed. Various refractoriness oil-soluble additive agents may be contained in microemulsion. Such materials are added so that it may have last physical properties or appearance with a specific polymer system and may be manufactured.

Although an example of such arbitrary oleophilic additive agents is not necessarily restricted, it contains what was chosen as this industry from a group which comprises a plasticizer like one sort of phthalic ester known well, supposing an oil phase is used — a standard [weight section / oil phase 100] — about 0 — about 20 weight sections — usually — being alike — about 5 — a plasticizer of about 8 — about 15 weight sections is included preferably about 20 weight sections.

[0051]In order to prepare surface-active agent microemulsion, it argues about the non-ion and ion (anion and cation) surface-active agent which are used for this invention below. A surface-active agent may be [which exist in microemulsion / the monomer and copolymeric], or may be non-copolymeric. As for a surface-active agent, it is preferred that it is copolymeric so that the polymer composite obtained may seldom become hypersensitivity in water. When the tolerance to water is unnecessary, a non-copolymeric surface-active agent is preferred from the Reason for the cost low generally.

1. A nonionic surface active agent nonionic surface active agent is usually a condensation product of the alkylene oxide which is organic aliphatic series or an alkyl aromatic hydrophobic compound, and hydrophilic nature, for example, ethylene oxide. it has the carboxy, hydroxy **, amide, or amino group in which the free water matter exists — all hydrophobic compounds are almost condensed with ethylene oxide, and a nonionic surface active agent can be formed. It is adjusted and deals in the length of the ethylene oxide chains of a condensation product so that desired hydrophobicity and the balance (hydrophilic-hydrophobic balance, i.e., HLB) of a hydrophilic component may be attained. HLB of a surface-active agent — the size of the hydrophilic nature (***** or polarity) of a surface-active agent, and a hydrophobic (***** or nonpolarity) basis, and the balance of strength — expressing . HLB of a nonionic surface active agent useful to this invention in order to prepare microemulsion — about 6 — about 19 — desirable — about 9 — about 18 — and it is about 10 — about 16 most preferably. A useful nonionic surface active agent contains what was chosen from the group which comprises the copolymeric nonionic surface active agents and those mixtures of the nonionic surface active agent of un-(**) polymerizing nature, and an ethylene system unsaturation.

[0052]1.a. A non-copolymeric nonionic surface active agent, especially the nonionic surface active agent of useful refractoriness, So that HLB specified above may be attained, although not necessarily restricted, Fatty alcohol containing high-class fatty alcohol of straight chain shape or the shape of a branched chain -, for example, about 8, and the carbon atom of 20 abbreviation, and about 3 - 100 mol of abbreviation, What is chosen from the group which comprises preferably the condensation product of about 5 - 40 mol of abbreviation which about 5 - ethylene oxide of 20 mol of abbreviation condensed most preferably is included. The examples of the ethoxylation fatty alcohol surface-active agent of such non-ion are the Tergitol(trademark)15-S series of Union Carbide, and a Brij (trademark) surface-active agent of ICI. A Tergitol(trademark)15-S surface-

active agent contains C_{11} - C_{15} secondary-alcohol polyethylene glycol ether. Brij(trademark)58 surface-active agent is polyoxyethylene (20) Sept lles ether, and Brij(trademark)76 surface-active agent is polyoxyethylene (10) stearyl ether. Other suitable refractoriness nonionic surface active agents so that HLB specified above may be attained, although not necessarily restricted, 1 mol of alkylphenol containing about 6-12 carbon atoms of straight chain shape or the shape of a branched chain and the thing which was preferably chosen [about 5 - 40 mol of abbreviation] from the group which comprises about 5 - a polyethylene oxide condensate with 20 mol of abbreviation most preferably as for the ethylene oxide 3 [about] - 100 mol of abbreviation are included. The example of a refractory nonionic surface active agent is Igepal(trademark) CO and CA series of Rhone-Poulenc. An Igepal(trademark) CO surface-active agent contains nonylphenoxypoly(ethyleneoxy) ethanol. An Igepal(trademark) CA surface-active agent contains octylphenoxypoly(ethyleneoxy) ethanol.

[0053] Another group of an usable refractoriness nonionic surface active agent, Although not necessarily restricted, what was chosen from about 6 - about 19, and the group that comprises preferably the block copolymer of about 9 - about 18, the ethylene oxide that has about 10 - about 16 HLB value most preferably and propylene oxide, or butylene oxide is included. The examples of such a non-ion block copolymer surface-active agent are Pluronic (trademark) of BASF, and a surface-active agent of Tetronic (trademark) series. A Pluronic (trademark) surface-active agent contains ethylene oxide propylene oxide block copolymer. A Tetronic (trademark) surface-active agent contains ethylene oxide propylene oxide block copolymer, being the further -- others -- the refractoriness nonionic surface active agent satisfied, although not necessarily restricted -- about 6 - about 19 -- desirable -- about 9 - about 18 -- and it has about 10 - about 16 HLB most preferably. What was chosen from the group which comprises a sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, and polyoxyethylene stearate is included. The examples of such a fatty-acid-ester nonionic surface active agent are Span (trademark) of ICI, Tween (trademark), and a Myrj (trademark) surface-active agent. A Span (trademark) surface-active agent contains C_{12} - C_{18} sorbitan monoester. A Tween (trademark) surface-active agent contains poly(ethylene oxide) C_{12} - C_{18} sorbitan monoester. A Myrj (trademark) surface-active agent contains polyethylene oxide stearate.

[0054]

1.b. A suitable nonionic surface active agent for making it contain in microemulsion of ethylene system unsaturation copolymeric nonionic surface active agent this invention is an ethylene system unsaturation copolymeric nonionic surface active agent, Although not necessarily restricted, it is general formula $R-O-(R'O)_m-(EO)_{(n-1)}-CH_2CH_2OH$ (among a formula). R (about -- about [C_2] -- C_{18} alkenyl, AKURIRIRU, and AKURIRIRU (about C_1 -about C_{10}) alkyl.) Methacrylyl, methacrylyl (about C_1 -about C_{10}) alkyl, It is chosen from a group which comprises a vinylphenyl and vinylphenylene (about C_1 -about C_6) alkyl, and; $R'O$ Two or more carbon atoms, It is chosen from a group which comprises an alkyleneoxy group of bivalence derived from an epoxy compound which has three pieces or four carbon atoms preferably, For example, propylene oxide, It is chosen from a group which comprises those mixtures, such as butylene oxide, and; E is ethylene of bivalence, m expresses about 5 - about 100 integer, n expresses about 5 - about 100 integer, and ratios of m to n are about 20:1 - abbreviation 1:20. What was chosen from a group which comprises an applicable thing is included. If a ratio of m and n is changed, HLB of a polymerizable surfactant will change. HLB required for a nonionic surface active agent of this invention is about 6 - about 19, and is about 9 - about 18 preferably, and is about 10 - about 16 most preferably. An example of such a copolymeric nonionic surface active agent is an alkylene polyalkoxyethanol surface-active agent, and is available at trade name Mazon BSN(trademark)185 from PPG Industries, and 186 and 187. A Mazon BSN (trademark) surface-active agent contains alkylene polyalkoxyethanol.

[0055]2. An anionic surface active agent anionic surface active agent, Usually, the hydrophobic part chosen from the group which comprises alkyl (about C_6 -about C_{20}), alkyl aryl, and an alkenyl group,

And sulfate, sulfonate, phosphate, polyoxyethylene sulfate, The anion group chosen from the group which comprises polyoxyethylene sulfonate, polyoxyethylene phosphate and the alkaline metal salt of such an anion group, ammonium salt, and the third class amino salt is included. As a hydrophobic part. (About C_2 -about C_{18}) In this invention the specific ethylene system unsaturation copolymeric surface-active agent containing the anion group of alkenyl polyoxypropylene or (about C_2 -about C_{18}) alkenyl polyoxy butylene, and polyoxyethylene sulfate. It is useful although microemulsion is manufactured. The further useful anionic surface active agent is described below to this invention.

[0056]2. the refractoriness anionic surface active agent which can be used in a. refractoriness anionic surface active agent this invention, Although not necessarily restricted, alkyl (about C_6 -about C_{20}), alkyl aryl sulfate, or sulfonate, For example, Sodium lauryl sulfate (as Polstep (trademark) B-3 from Stepan Co.) Marketing and sodium dodecylbenzenesulfonate (it markets as Siponate(trademark) DS-10 from Rhone-Poulenc); They are polyoxyethylene (about C_6 -about C_{20}) alkyl or alkylphenol ether sulfate, The ethylene oxide repeating unit in a surface-active agent is less than about 30 units, What is preferably less than about 20 units, and is most preferably less than about 15 units, For example, Polstep of marketing from StepanCo. (Trademark) B-1, Ailpal (trademark) EP110 of Rhone-Poulenc, and 115; They are the alkyl (about C_6 -about C_{20}) of phosphoric acid or alkyl phenoxypropyl(ethyleneoxy) ethylmonoester, diester, and its salt, The ethylene oxide repeating unit in a surface-active agent contains what was chosen from the group which comprises the thing which is less than about 30 units, is preferably less than about 20 units, and is most preferably less than about 15 units, for example, Gafac(trademark) PE-510 of GAF, and Gafac(trademark) RE-610.

[0057]

2.b. The suitable anionic surface active agent for making it contain in the microemulsion of ethylene system unsaturation copolymeric anionic surface active agent this invention is formula $R-O-(R'O)_m-(EO)_{n-1}-CH_2CH_2X$, although not necessarily restricted. the inside of [type, and R (about — about $[C_2-]$ — the C_{18} alkenyl —) [AKURIRIRU and] AKURIRIRU (about C_1 -about C_{10}) alkyl, methacrylyl, It is chosen from the group which comprises methacrylyl (about C_1 -about C_{10}) alkyl, a vinylphenyl, and vinylphenylene (about C_1 -about C_6) alkyl, and;R'O Two or more carbon atoms, The alkyleneoxy group of the bivalence derived from the epoxy compound which has three pieces or four carbon atoms preferably, For example, it is chosen from the group which comprises mixtures of such an alkyleneoxy group, such as propylene oxide and butylene oxide, and;E is ethylene of bivalence,m expresses about 5 – about 100 integer,n expresses about 5 – about 100 integer, and the ratios of;m to n are about 20:1 – abbreviation 1:20. What was chosen from the group which comprises the ethylene system unsaturation copolymeric surface-active agent of] is included. If the ratio of m and n is changed, HLB of a polymerizable surfactant will change. HLB required for the anion copolymeric surface-active agent of this invention is about 3 – about 16 except for X-basis. X is the anion group chosen from the group which comprises the alkaline metal salt, the ammonium salt, or the third class amino salt of sulfonate, sulfate, phosphate, and such an anion group. The example of such a copolymeric anionic surface active agent is Mazon(trademark) SAM 211 of PPG Industries and Inc. [0058]1. In cationic surface active agent this invention a useful cationic surface active agent, Although not necessarily restricted, what was chosen from a group which comprises quarternary ammonium salt in which a basis of a lower molecular weight of a basis of a higher molecular weight of at least one piece and two pieces, or three pieces combined with a common nitrogen atom, and formed a cation is included. Here, an anion made to balance electrically is chosen from a group

which comprises halogenides (a bromide, a chloride, etc.), acetate, nit RITTO, and low-grade ARUKO sulfate (METOSURU Fet etc.). a substituent of the amount of polymers is often a higher alkyl group from that on nitrogen — about 10—, including about 20 carbon atoms, More, the substituent of low molecular weight can be low-grade alkyl, for example, methyl, or ethyl of a carbon atom of about 1 — four abbreviation, and it may be replaced by hydroxy **, for example depending on the case. One or more substituents may also contain an aryl portion, and it may be replaced by aryl, for example, benzyl, and a phenyl. about 1— it being low-grade alkyl, for example, methyl, or ethyl of about four carbon atoms, being replaced by low-grade polyalkoxy portion like a polyoxyethylene portion, and, including a hydroxy end group, A thing applicable to general formula— $R(CH_2CH_2O)_{(n-1)}CH_2CH_2OH$ (—R is an alkyl group of bivalence of C_{1-4} combined with nitrogen among a formula, and n expresses about 1 — about 15 integer.) is contained in a possible low-molecular-weight substituent.

Independently, it is not combined with quaternary nitrogen through the above-mentioned low-grade alkyl, but 1 of such a low-grade polyalkoxy portion that has hydroxyl of an end, or two pieces may couple directly with quaternary nitrogen. An example of a quaternary ammonium halide surface-active agent useful to use by this invention, Although not necessarily restricted, it is methylbis(2-hydroxyethyl)****- ammonium chloride or oleyl ammonium chloride (respectively) from Akzo Chemical Inc. What was chosen from a group which comprises Ethoquad(trademark) C/12, O/12, and methylpolyoxyethylene (15) octadecyl ammonium chloride (Ethoquad(trademark) 18/25) is included.

[0059]The typical constituent concentration (weight %) in the microemulsion of this invention is as in the following table 1.

[0060]

[Table 1]

マイクロエマルジョン	有用	好適	最好適
親水性モノマー	15—85%	25—75%	30—65%
水	2—40%	5—50%	8—40%
極性種	2—80%	5—50%	8—40%
界面活性剤	5—70%	7—50%	9—35%

[0061]Each numerical value in Table 1 shows a rough value. These figures express weight % to the gross weight of microemulsion. The concentration of each ingredient is selected so that the whole may be 100%.

[0062]Since microemulsion forms spontaneously the manufacturing method of the microemulsion of manufacturing method this invention of microemulsion, without needing most intense stirring, it is comparatively easy. However, it is desirable to dissolve an oil-soluble photoinitiator in a hydrophobic monomer beforehand, and to dissolve beforehand all the water-soluble additive agents, an oil insolubility ionicity monomer, or a water-soluble photoinitiator in water, and to form a solution. Subsequently, the transparent and homogeneous microemulsion which does not carry out phase separation even if it mixes with a polar monomer, a surface-active agent, and other additive agents of all the and carries out aging of this hydrophobic monomer mixture and solution is manufactured. It is not necessary to use heat and almost all mixing processes are mostly carried out suitably at a room temperature (20—30 **).

[0063]The phase transition between the transparent microemulsion of a 1 phase system of this invention and the emulsion in which the two phase system became muddy is shown in drawing 1 — drawing 3. These are only illustration although these figures show the three phase figure about a hydrophilic pile affinity phase, a hydrophobic pile affinity phase, and the concentration of a surface-active agent (polymerization nature or non-polymerizable) about a certain specific microemulsion.

[0064] Drawing 1 is a phase diagram showing a microemulsion field transparent about the desirable constituent of this invention, and the emulsion field which became muddy. In this constituent, from PPG Industries, a surface-active agent is polymerization nature anionic surface active agent and Mazon (trademark) SAM211 marketed, and the heavy affinity phase of hydrophilic nature, It is a mixture which contains polyoxyethylene acrylate (PEOA), deionized water, and potassium chloride by the weight ratio 68:30:2, and a hydrophobic heavy affinity phase is a mixture which contains isobornyl acrylate and acrylic acid by the weight ratio 85:15. The slash field of drawing 1 shows the density range where the useful microemulsion by this invention was obtained.

[0065] Drawing 2 is a phase diagram showing a microemulsion field transparent about the desirable constituent of this invention, and the emulsion field which became muddy. The non-polymerizable nonionic surface active agent in which the surface-active agent is marketed from Union Carbide in this constituent, Are Tergitol15(trademark)-S-12 and the heavy affinity phase of hydrophilic nature, It is a mixture which contains polyoxyethylene acrylate, deionized water, and potassium chloride by the weight ratio 68:30:2, and a hydrophobic heavy affinity phase is a mixture which contains isobornyl acrylate and acrylic acid by the weight ratio 85:15. The slash field of drawing 2 shows the density range where the useful microemulsion by this invention was obtained.

[0066] Drawing 3 is a phase diagram showing a microemulsion field transparent about the desirable constituent of this invention, and the emulsion field which became muddy. In this constituent, surface-active agents are a non-polymerizable cationic surface active agent, and Ethoquad (trademark) C/12, and the heavy affinity phase of hydrophilic nature, It is a mixture which contains polyoxyethylene acrylate, deionized water, and potassium chloride by the weight ratio 68:30:2, and a hydrophobic heavy affinity phase is a mixture which contains isobornyl acrylate and N-vinyl pyrrolidone by the weight ratio 85:15. The slash field of drawing 3 shows the density range where the useful microemulsion by this invention was obtained.

[0067] If microemulsion is obtained, a radical polymerization will be made to start and a polymerization will be made to cause by irradiating a person skilled in the art with an electromagnetism radiant ray by a well-known technique. After applying microemulsion on a flexible carrier web by one means of the daily use, such as roller coating, dip coating, knife coating, or extrusion coating, In an inert atmosphere (namely, atmosphere which does not contain oxygen), using a nitrogen atmosphere as everyone knows etc. polymerizes in the technical field concerned.

[0068] The plastic film which does not penetrate oxygen although ultraviolet rays are penetrated substantially, After combining microemulsion with the polyester film which has a silicone series remover on the surface which contacts microemulsion preferably, Microemulsion can also be polymerized in the air by using the fluorescence type ultraviolet ray lamp which emits the UV light of the wavelength range which the used photoinitiator absorbs, and irradiating with microemulsion through this film. Several kinds of lamps marketed can be used. A medium-voltage mercury-vapor lamp and a low-strength fluorescent lamp are in these, and it has various kinds of emission spectra, respectively, and the luminescence maximum is shown among 280-400 nm. It is preferred to use the fluorescence black light of marketing which has 90% of luminescence in the range which is 300-400 nm for convenience, and has the maximum in about 351 nm.

[0069] Generally, the total exposure dose should be made about $200-700 \text{ mm J } [/\text{cm}]^2$. The maximum efficiency and speed of a polymerization are shown by the used expression of relations of the absorption feature of a photoactive compound, and the radiation property of an irradiation source. When the 2,2-dimethoxy-2-phenyl-acetophenone (known also as 2,2-dimethoxy-2-phenyl-1-phenylethanone and benzyl dimethyl ketal) which is a desirable photoinitiator is used, It is preferred that it is while not less than about 75% of radiant rays are 300-400 nm.

[0070] Although photopolymerization can also be carried out in an inert atmosphere, it can raise the admissibility for oxygen by making an oxidizability tin compound contain in a constituent as it writes in the US,4,303,485,B Description. As one of the photopolymerization method, after average light

intensity irradiates microemulsion with the electromagnetism radiant ray of $0.01\text{--}20\text{ mW } [\text{J}/\text{cm}^2]$ at about $280\text{--}500\text{ nm}$ first in wavelength, There is a way wavelength irradiates with the electromagnetism radiant ray whose average light intensity is higher than $20\text{ mW } [\text{J}/\text{cm}^2]$ at about $280\text{--}500\text{ nm}$.

[0071]Desirable photopolymerization method is sufficient method of carrying out a time exposure and giving about $680\text{ mm J } [\text{J}/\text{cm}^2]$ about microemulsion in about 351-nm electromagnetism radiant ray. In this case, the photopolymerization time for about 10 minutes is required. Even if it gives continuously by the requirements for manufacture, the amount of ultraviolet energies which irradiates with this microemulsion is batch-like, and may be given. Microemulsion may be polymerized under ambient conditions. Ambient air temperature, ambient pressure, and ambient humidity are permissible.

[0072]If a polymerization is completed, superfluous moisture may be removed with the evaporation method which uses a convection furnace and the source of infrared rays if needed.

The conductivity of polymer was measured by the measure resistance method of the four measuring method probe type of the examining method conductivity. Four metallic pins which kept the equal interval $D\text{ (cm)}$ were pressed against the polymer sample with the spring. The current of the intensity $I\text{ (ampere)}$ was sent through the outside pin. The amount V of voltage drops between inside probes (bolt) was measured. Resistivity is computed by a lower formula.

Resistivity (Ωcm) = $2\pi IDV/I$ conductivity is computed by a lower formula.

Conductivity = $1 / \text{resistivity}$ Reference documents : L. J. van der Pauw, Philips Res. Repts. 16 (1961) 187; J. Hornstra and L. J. van der Pauw, J. Electronics and Control 7 (1959) 169. [0073]The following cable addresses and trademarks are used on the cable address and the trademark book Descriptions.

Comp. ; comparative example DI water; — deionized water IBOA; — isobornyl acrylate IOA ; Isooctyl acrylate MMA ; methyl methacrylate AA; — acrylic acid NVP ; N-vinyl pyrrolidone AcM ; Acrylamide KAA. ; Acrylic acid potassium MazonTMSAM. 211 ;P PG. Alkylene polyalkoxy sulfate surface-active agent KCI made from Industries ; Potassium chloride PEOA; poly (ethylene oxide) acrylate or poly (oxyethylene) acrylate M.W., [Molecular weight TergitolTM15-S-12;] Union.

Ethoxylated fatty alcohol surface-active agent TexaponTM L100 made from Carbide ; Sodium-lauryl-sulfate surface-active agent SaponateTMDS10 made from Henkel ; Dodecylbenzenesulfonic acid made from Rhone-Poulenc. The ammonium alkylphenol made from alkyl poly(ethyleneoxy) ethyl phosphate surface-active agent PolystepTMB-1;Stepan Chemical made from sodium surface-active agent GafacTMRE610;GAF. The ammonium alkylphenoxy poly(ethyleneoxy)ethanol sulfate surface-active agent made from ethoxy rate sulfate surface-active agent AlipalTMEP110;Rhone-Poulenc [0074]

[Working example]Although the following embodiments explain this invention further, these embodiments do not limit this invention. Unless it refuses in particular, all of these embodiments and the part in the Description remainder, percent, a ratio, etc. are based on weight.

One to embodiment 6 Embodiments 1-6 carry out the microemulsion which has the aqueous phase (hydrophilic phase) and oil phase (canal phase) of the polymerization nature manufactured with polymerization nature and a non-polymerizable anionic surface active agent example 1.

[0075]The solution which contains 0.5 g of potassium chloride (KCl) in 7.5 g of deionized water in the jar of 1200 ml of embodiments was prepared at the room temperature. 9.4 g of acrylic acid (AA) and 22.2 g of poly (ethylene oxide) acrylate (PEOA) were added to this solution, and the hydrophilic phase was prepared. Subsequently, 48.0 g of isobornyl acrylate (IBOA) and MazonTMSAM 211 12.5-g surface-active agent were mixed to the hydrophilic phase, and transparent microemulsion was obtained.

The microemulsion of two to embodiment 6 Embodiments 2-6 was prepared like Embodiment 1 except for having used the ingredient and quantity which were displayed on the following table 2 instead of the ingredient and quantity which were indicated in the Embodiment 1.

[0076]

[Table 2]

実施例	重量 %					
	1	2	3	4	5	6
IBOA	48.0	35.5	33.4	32.9	32.5	31.8
AA	9.4	8.1	---	5.8	5.7	5.5
NVP	---	---	16.5	---	---	---
PEOA***	22.2	27.8	22.7	26.4	26.0	24.8
脱イオン水	7.4	12.2	10.0	11.6	11.4	10.9
KCl	0.5	---	0.7	0.8	0.7	---
Mazon™ SAM211*	12.5					
Texapon™ L100*		18.4				
Siponate™ DS10*			16.7			
Polystep™ B-1*				22.5		
Alipal™ BP110*					23.7	
Gafac™ RB610*						27.0

[0077]* All percents are based on the gross weight of microemulsion.

* Before using the anionic surface active agent of *Polystep™ B-1 and Alipal™EP110 for preparation of microemulsion, it dried within a 105 °C furnace for about 10 to 15 hours, and it made activity 100%. The anionic surface active agent of Mazon™SAM 211, Texapon™ L100, Siponate™DS10, and Gafac™RE610 was used as it was. Mazon™SAM 211 is a copolymeric anionic surface active agent. Texapon™ L100, Siponate™DS10, Polystep™ B-1, Alipal™EP110, and Gafac™RE610 are non-copolymeric anionic surface active agents.

* Number average molecular weight =750 of ** PEOA [0078]Seven to embodiment 14 Embodiments 7-14 illustrate the process of the microemulsion which has the aqueous phase (hydrophilic phase) and oil phase (canal phase) of the polymerization nature manufactured with the copolymeric and non-copolymeric nonionic surface active agent. These microemulsion was prepared like Embodiment 1 except for having used the ingredient and quantity which were displayed on the following table 3 instead of the ingredient and quantity which were indicated in the Embodiment 1.

[0079]

[Table 3]

実施例	重量 %							
	7	8	9	10	11	12	13	14
IBOA	47.1	46.1	47.4	42.6	44.8	39.4	44.1	47.4
AA	9.3	9.0	9.2	8.3	8.7	7.7	8.6	9.2
PBOA***	23.5	22.8	23.3	21.1	22.1	19.5	21.9	23.3
脱イオン水	5.8	5.7	5.8	5.3	5.5	4.9	5.5	5.8
KCl	0.5	0.5	---	0.5	0.5	0.4	0.5	0.5
BSN™ 186*	13.8							
Igepal™ CAG30*		15.9						
Tergitol™ 15-S-12*			14.3					
Pluronic™ L64*				22.2				
Tetronic™ 1304*					18.4			
Tween™ 20*						19.2		
Myrj™ 52*							19.2	
Brij™ 58*								13.8

[0080]* All percents are based on the gross weight of microemulsion.

** BSN™186 is a copolymeric nonionic surface active agent made from PPG Industries. It was then used (that is, it does not dry before use).

The remaining nonionic surface active agents of Table 3 are non-copolymeric nonionic surface active agents, and were used as it was also about these (that is, it does not dry before use).

* Number average molecular weight =750 of ** PEOA [0081]Embodiment 15 and 16 Embodiments 15 and 16 illustrate the process of the microemulsion which has the hydrophilic phase and canal phase of the polymerization nature manufactured with the non-copolymeric cationic surface active agent. Although these microemulsion was prepared like Embodiment 1, it used the ingredient and quantity which used N-vinyl pyrrolidone (NVP) instead of and were moreover displayed on the following table 4. [acrylic acid]

[0082]

[Table 4]

実施例	重量 % *	
	15	16
IBOA	31.3	35.6
NVP	8.0	7.1
PEOA***	14.7	31.3
脱イオン水	15.3	3.6
KCl	---	0.7
Rthoquad™ C/12*	30.7	
Rthoquad™ 18/25*		21.7

[0083]* All percents are based on the gross weight of microemulsion.

** cationic surface active agent was used as it was (that is, it does not dry before use).

* Number average molecular weight =750 of ** PEOA [0084]The following Embodiments 17-25 explain the process of the polymer composite which has the double continuation structure by the polymerization of microemulsion.

The solution which contains 0.5-g KCl in 8.8 g of deionized water in the jar of 17200 ml of process embodiments of the polymer which has the double continuation structure by the polymerization of microemulsion was prepared at the room temperature. 9.4 g AA and 20.8-g PEOA were added to this solution, and the hydrophilic phase was made to form. Subsequently, 47.7 g IBOA,

MazonTMSAM211 12.5 g surface-active agent, and a 0.3-g benzyl dimethyl ketal photoinitiator were mixed to this hydrophilic phase, and transparent microemulsion was obtained to it. Then, this transparent microemulsion was poured in into the 5cmx15cmx2mm cell demarcated with the glass of the couple which has a release liner. Subsequently, the cell containing microemulsion was irradiated with the product [made by General Electric] F40BL type 40-W UV light which generates 1.9mJ from the place distant 6 cm for 20 minutes at the room temperature, and the polymerization was made to cause. After the polymerization, according to the four-point probe type measure resistance method, as shown in Table 5, the polymer solid showed conductivity, and it suggested that polymer composite had taken double continuation structure.

[0085]In Embodiments 18-24, the ingredient indicated to Table 5 in accordance with the above-mentioned method was mixed, and microemulsion was prepared, and solid polymer was prepared from the microemulsion. Polymer of hydrophilic nature, the adhesiveness by hydrophobic double continuation polymer composite, and non cohesiveness was manufactured by this method.

The comparative example 25 comparative example 25 illustrates the process of polymer which is not double continuation. Although the procedure of Embodiment 17 was adopted, however since deionized water was excluded, microemulsion was not formed. The obtained polymer was non-conducting intrinsically, as shown in Table 5.

[0086]

[Table 5]

実施例	重量 % *								
	17	18	19	20	21	22	23	24	比較例25
IBOA	47.7	56.1			22.5		48.3	48.8	47.7
IOA			50.9	48.2	22.5				
NMA						45.2			
ベンジルジメチルケタール	0.3	0.5	0.5	0.5	0.3	0.8	0.5	0.5	0.3
脱イオン水	8.8	6.0	10.0	7.7	8.5	8.5	11.3	9.5	
KCl	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PEOA***	20.8	23.0		22.3	20.0	20.0			20.8
AA	9.4		12.4		9.0	9.0		11.5	9.4
NVP				7.8					
AcM								2.5	
KAA							13.3		
Mazon SAM TM 211	12.5	13.8	25.7	15.0	16.0	16.0	26.1	26.7	12.5
*導電率×10 ⁻⁷	22	170	263	197	12	5	10	112	0.06

[0087]* All percents are based on the gross weight of microemulsion.

* Number average molecular weight =750 of $\omega^{-1}\text{cm}^{-1}$ *** PEOA [0088]The form of the polymer which might be followed by Embodiments 17 and 24 was observed by scanning electron microscope SEM (Bedford, goods Amray 1810 microscope marketed from Amray of MA.). Freeze fracturing of the sample is carried out in liquid nitrogen, And sputtering coating of the golden-palladium was carried out for 4 minutes at 10 kV using the sputtering system (Agawam, goods Ultra-Spec 90 LVC sputtering system marketed from Energy Beam Sciences of MA.). Magnification was made into 3000 or more times.

[0089]Drawing 4 shows the SEM microphotograph of polymer of Embodiment 17. Polymer of Embodiment 17 is flexible non cohesiveness polymer which has a nonporous form substantially. 0.1 micrometers or more in diameter a stoma or open space were not accepted at all, but polymer was nonporosity substantially. Drawing 5 shows the SEM microphotograph of polymer of Embodiment 24. Polymer of Embodiment 24 is non cohesiveness polymer without the pliability which has a nonporous form substantially. 0.1 micrometers or more in diameter a stoma or open space were not accepted at all, but polymer was nonporosity substantially.

[0090]Polymer of Embodiment 24 was prepared by the heat induction polymerizing method by the method indicated in the embodiment of the US,5,238,992,B Description (Outubuddin) for comparison. This polymer composite was non cohesiveness polymer without the pliability in which the big bubble was confined inside. It filled up, so that open space could not be permitted in this polymer, and it was not nonporosity substantially.

[0091]Although this invention was explained in connection with a special embodiment, please understand that it can change further. The Claims in this Description include such all transformation to be accepted if it is a person skilled in the art as it is chemically as equal as what was indicated here.

[Translation done.]

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TECHNICAL FIELD

[Industrial Application] This invention relates to the polymer material which has a nonporous double continuation structure substantially. A nonporous double continuation (bicontinuous) structure is the structure where both of hydrophilic polymer phases and hydrophobic polymer phases are continuing, and each phase moreover shows each bulk properties, substantially. This invention relates also to the manufacturing method of the microemulsion to which a radical polymerization nature monomer exists in both the aqueous phase and an oil phase, and such microemulsion, and the method of reaching and manufacturing a polymer material.

[Translation done.]

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PRIOR ART

[Description of the Prior Art]A surfactant mixture with suitable microemulsion They are water / oil system colloidal dispersion object stable with [a surface-active agent usually like soap and an auxiliary surface-active agent (cosurfactant) like short chain alcohol]. In contrast with the turbidity emulsion of custom in which stability originates in kinetics purely, microemulsion is thermodynamically stable and is spontaneously formed by contact. It is one with a small (about 10 nm) size of the globular form droplet currently distributed in a continuation medium, and is optically transparent. Encyclopedia of Polymer Science Engineering, Wiley: Please refer to New York 1987 Vol. 9 and p.718.

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TECHNICAL PROBLEM

[Problem to be solved by the invention] In the technical field concerned, neither polymer which has a nonporous double continuation structure substantially also being manufactured, nor needs for such polymer are recognized. These polymer that has a nonporous double continuation structure substantially, A hydrophilic polarity kind of radical polymerization nature contained in an aqueous (water) phase of microemulsion and a hydrophobic monomer of radical polymerization nature contained in an organic (oil) phase are polymerized simultaneously, and it is obtained by forming polymer which has two sorts of solids which have a nonporous double continuous phase substantially.

[0013] Such polymer that has a nonporous double continuation structure substantially has the useful bulk properties of both hydrophilic polymer and a hydrophobic polymer for especially a use searched for. For example, to moisture and/or bacteria, while it is impermeableness, a breathable film with the high transportability of a steam is desired dramatically. In such polymer, either a hydrophobic substance or a hydrophilic substance can be caught or released gradually. Material in which another bulk properties of one side of a phase or both have an advantage demonstrated simultaneously can also be manufactured. For example, adhesive acrylate type adhesives made into conductivity can be manufactured by making a hydrophilic phase contain an electrolyte.

[0014] This invention provides a formation method of microemulsion in which a solid contains both a manufacturing method of a nonporous double continuation polymer material and such a material, and a hydrophilic radical polymerization nature polarity kind and a hydrophobic radical polymerization nature monomer substantially, and such microemulsion.

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MEANS

[Means for solving problem]Polymer composite of this invention includes an optical start polymerization product of microemulsion which has a nonporous double continuation structure substantially and has aqueous phase and an oil phase. said microemulsion -- the following -- (a) - the (e):(a) water 2 [about] - about 40 weight %; (b) the radical copolymeric ethylene system unsaturation polarity kind 2 [about] - about 60 weight %; (c) the radical copolymeric ethylene system unsaturation hydrophobic monomer 15 [about] - about 85 weight %; (d). Do not carry out copolymerization to a polar kind of (1) ingredient (b), and a monomer of an ingredient (c). A nonionic surface active agent, a cationic surface active agent, anionic surface active agents, and these mixtures, (2). Copolymerization can be carried out to a polar kind of an ingredient (b), and a monomer of an ingredient (c). An ethylene system unsaturation nonionic surface active agent, a cationic surface active agent, anionic surface active agents and these mixtures, the surface-active agent 5 [about] chosen from a group which comprises both (3), (1), and (2) - about 70 weight %; and the (e) oleophilic photoinitiator 0.01 [about] - about 5 weight sections; It includes [however, the amount of photoinitiators of (e) is based on gross weight of the above (a), (b), (c), and (d) for weight % of the above (a), (b), (c), and (d) on the basis of gross weight of microemulsion, respectively]. Said both of polymerization products have a double phase of double continuation structure which is a nonporous solid substantially.

[0016]The unique double continuation polymer system of this invention is acquired as a result of carrying out the simultaneous polymerization of the radical pile affinity kind in both the aqueous phase of microemulsion, and an organic phase. At the time of the simultaneous polymerization in each phase, the aqueous phase and an organic phase live together in the state of the mutually united continuation domain. They are double continuity.

[0017]In this way, while the polymerization in the aqueous phase brings about the hydrophilic polymer which has hydrophilic bulk properties, the polymerization in an oil phase brings about the hydrophobic polymer which has hydrophobic bulk properties. Since a simultaneous polymerization takes place, the polymer composite of nonporosity substantially which has both hydrophilic polymer and a hydrophobic polymer is obtained. There is that no one of polymer serves as a disperse phase substantially, it lives together as a domain where both of the polymer continued substantially, and the composite material obtained as a result serves as nonporosity and double continuity substantially. This polymer composite has two solid phases, and one hydrophilic polymer and the hydrophobic polymer of another side live together as a nonporous double continuation structure substantially.

[0018]Although not limited to a specific theory, the polymer composite of this invention has both a hydrophobic continuous phase and a hydrophilic continuous phase as a form formed when microemulsion is polymerized. A hydrophobic continuous phase is formed when a hydrophobic

monomer polymerizes, and a hydrophilic continuous phase is formed when a hydrophilic monomer polymerizes. The microemulsion constituent produced by polymerizing shows the characteristic with both hydrophilic nature which followed the continuous hydrophobicity, and can perform neither of things for which the solvent of a hydrophobic polymer also dissolves the microemulsion constituent produced by the solvent of hydrophilic polymer polymerizing.

[0019]***** [that there are the independent hydrophobic polymer and hydrophilic polymer which are together put at the time of a polymerization so that the mechanical concentration which can resist a solvation may be formed]. About whether copolymerization is carried out, some do not understand the hydrophobic monomer and the hydrophilic monomer at present so that a hydrophobic monomer and a hydrophilic monomer may form concentration of chemical share nature in the field which carried out copolymerization.

[0020]Even if the form of the polymer composite of this invention is a case where an exact form cannot describe with a molecular level, one side of a phase is distributing and another side differs from the two phase form composite material which is continuation. The constituent of this invention is because the bulk properties by the continuity of a hydrophobic polymer phase and the bulk properties by the continuity of a hydrophilic polymer phase are compatible. "Double continuation structure" is a term for describing the form of the microemulsion after the polymerization with which the characteristic by a hydrophobic continuous phase and the characteristic by a hydrophilic continuous phase are compatible.

[0021]The method of this invention is also important for the form of the polymer composite obtained. A mixture remains as microemulsion stable at the time of a polymerization, and in order for the polymer composite moreover obtained to show structure concentration nature, both of the monomers of a kind need to polymerize promptly. The quick and controllable polymerizing method which makes it possible to keep ["freezing" or] the form of microemulsion stable, and to stop the phase separation of microemulsion to the minimum, and to obtain nonporous polymer composite substantially in the case of a polymerization is a radical polymerization method which uses a photoinitiator and an electromagnetism radiant ray. Although it is possible as comparison to form nonporous polymer composite substantially under the heat start radical polymerization conditions using the monomer illustrated by the US,5,238,992,B Description (Outubuddin) under a certain kind of conditions, There is a limitation in the capability for a thermal initiation to be controllable. Since control of polymerization reaction speed is difficult, by the heat induction polymerizing method, there is a possibility that the form of the polymer composite obtained may change. Since this invention tends to control the direction which the form of the microemulsion in the case of a polymerization (microemulsion after the polymerization obtained if it lengthens) depends on the optical starting method compared with the heat starting method and can attain the form of a request of the polymer composite of this invention, photopolymerization method is used for it.

[0022]If the optical start polymerizing method is adopted as an unexpected thing, a nonporous composite material will be formed certainly substantially [request / of this invention]. In order for the Reason which photopolymerization method can trust dramatically to start a polymerization, it is not necessary to change temperature. photopolymerization method stops [that a polymerization is controllable (for example, the case where the electromagnetism radiant ray is irradiated — as long as — a polymerization takes place), and] the phase separation of the microemulsion at the time of photopolymerization to the minimum — it comes out.

[0023]The US,5,238,992,B Description will have indicated that a porosity polymer blend and a composite material are formed preferentially, if the heat start polymerizing method is used. This invention is not the heat start polymerizing method, and eliminates a porous blend and composite material by providing the polymer composite which was prepared with photopolymerization method and which has a nonporous double continuation structure substantially.

[0024]The term "it is nonporosity substantially" in this Description means that the stoma or open space in a composite material does not exist on the level which exceeds 0.1 micrometer in diameter.

"It is nonporosity substantially", The US,5,238,992,B Description and "Preparation and Characterization of Porous Polymers from Microemulsions" (ACS.) of Qutubuddin and others Chapter 5 of Symposium Series384, It is clearly distinguished from the porous structure in the micrometer level indicated to Polymer Association Structures, American Chemical Society, and 1989.

[0025]The aqueous phase is provided with the following.
Water.

At least one sort of radical copolymeric ethylene system unsaturation polarity kinds, for example, a monomer, and/or oligomer.

This aqueous phase if needed A refractoriness polarity oligomer additive agent, a radical polymerization nature photochemistry activation cross linking agent, One or more sorts of ingredients chosen from the group which comprises an auxiliary solvent, a water-soluble radical photopolymerization initiator, a water-soluble radical thermal initiator, and (it is (like the additive agent chosen from the group which comprises an electrolyte, a color, and a substance [activity / in drugs])) a water-soluble functional additive agent can be included further.

[0026]The term "polarity" in this Description means the kind in which a measurable dipole moment is shown, and the term "oligomer" means the polymer kind which has a repeating unit to about 2000 pieces by two or more pieces and the maximum.

[0027]An organic phase contains the ethylene system unsaturation hydrophobic monomer of at least one sort of radical polymerization nature, the ethylene system unsaturation polar monomer of radical polymerization nature, and an oil-soluble radical photopolymerization initiator. The oil-soluble cross linking agent which this organic phase can contribute to the bulk properties of a refractoriness polarity oligomer additive agent and the constituent obtained if needed. One or more sorts of ingredients chosen from the group which comprises an oil-soluble chain transfer agent, an oil-soluble radical thermal initiator, and (as [chose / out of the group which comprises a plasticizer, a color, a substance / activity / in drugs /, and a tackifier]) an oil-soluble functional additive agent can be included further.

[0028]The third basic component of microemulsion is a surface-active agent of nonionic or ionicity (an example, anionic, or cationicity), and the compatibility that can be anionic or nonionic preferably. If suitable, it will dissolve in neither an organic phase nor the aqueous phase, but the additive agent and bulking agent (for example, a web, scrim or silica, activity carbon black, or a fibrous filler) by which it is arranged inside the last polymer composite which has a nonporous double continuation structure substantially and in which it deals may be made to contain.

[0029]Even if it mixes the ingredient which composes the aqueous phase, an organic phase, and a surface-active agent in which order, transparent microemulsion forms spontaneously. Subsequently, carry out the cast of the microemulsion into a suitable metallic mold, may irradiate with an electromagnetism radiant ray, may carry out a radical polymerization promptly, and. Apply microemulsion on a base material, on the base material, may irradiate with an electromagnetism radiant ray, may carry out a radical polymerization promptly, and, Or the cast of the microemulsion may be carried out so that a sheet or the reinforcement of mesh state, for example, scrim etc., may be included, and it may irradiate with an electromagnetism radiant ray, and a radical polymerization may be carried out promptly. in these various methods — "quick" — it means that a polymerization takes place so that a nonporous double continuation structure may be substantially acquired in polymer composite, without the form of microemulsion changing substantially in the case of a polymerization.

[0030]Preferably, electromagnetism radiant rays are ultraviolet rays which activate the photoinitiator in microemulsion and enable the monomer in microemulsion, and/or the simultaneous polymerization of oligomer. Obtained polymer composite which has a nonporous double continuation structure substantially can be made into adhesiveness and print resistance by operation of the used hydrophobic monomer. This whole system characteristic can be adjusted with the ingredient in both

the aqueous phase and an organic phase.

[0031]A nonporous double continuation structure can be inspected with a scanning electron microscope substantially [polymer composite / of this invention]. In a micron and a submicron level, as it is in the scanning electron microscope photograph of drawing 4, for example, it turns out that there is not a stoma or open space into the polymer composite of this invention.

[0032]The feature of this invention is at the point that the bulk properties of hydrophilic polymer (it polymerizes in the aqueous phase of microemulsion) and the bulk properties of a hydrophobic polymer (it polymerizes in the oil phase of microemulsion) live together. Another feature of this invention has a composite material of this invention in improving the conventional hydrophobic polymer with the bulk properties of hydrophilic polymer, and the point which makes the reverse possible.

[0033]The advantage of this invention is that neither of the phases of polymer composite is the disperse phases in which continuity has broken off in the composite material. Another advantage of this invention is that the quick optical start polymerizing method brings about nonporous polymer composite substantially.

[0034]I. Before an aqueous-phase polymerization start, the aqueous phase of microemulsion contains a water-soluble additive agent a water-soluble initiator and if needed water, the ethylene system unsaturation polarity kind of radical (**) polymerization nature, and if needed.

I.a. the microemulsion of Mizumoto invention -- the gross weight standard of microemulsion -- about 2- about 40 weight % -- desirable -- about 5- about 30 weight % -- and -- most -- desirable -- about 6- about 20weight % of water is included. Preferably, microemulsion contains deionized water.

[0035]I.b. the aqueous phase of ethylene system unsaturation polarity Tanemoto invention of radical (**) polymerization nature -- water -- in addition, include the ethylene system unsaturation polarity kind of radical polymerization nature. Polar monomers other than the monomer such whose a polar kind is insolubility substantially in an oil phase, and an oil insolubility monomer. It is chosen from (namely, the monomer which are water solubility and oil solubility), and the group which comprises polar oligomer (namely, oligomer which is hydrophilic oligomer or water solubility, and oil solubility which are insolubility substantially in an oil phase). Such a monomer is chosen from the group which comprises polar monomers (namely, water solubility and an oil-soluble monomer) other than the polar monomer which is insolubility substantially, and an oil insolubility monomer in an oil phase.

[0036]microemulsion -- character of a request of polymer composite -- a gross weight standard of microemulsion -- about 2- about 60 weight % -- desirable -- about 5- about 50 weight % -- and -- most -- desirable -- about 8- about 40weight % of a required polar kind is included cumulatively.

I.b.i. it is insolubility substantially in a polar ethylene system unsaturation radical (**) polymerization nature oligomer oil phase. Or useful polar ethylene system unsaturation radical (**) polymerization nature oligomer which is water solubility and oil solubility, Although not necessarily restricted, polyethylene oxide acrylate, polyethylene oxide diacrylate, What was chosen from a group which comprises polyethylene-glycol acrylate, polyethylene-glycol diacrylate, polyurethane acrylate, polyurethane diacrylate, N-vinyl-pyrrolidone macromere, and those mixtures is included.

Polyethylene oxide acrylate and diacrylate are preferred. The most desirable oligomer contains polyethylene oxide acrylate from a Reason of acquisition ease and combination ease. Useful oligomer for the optimal physical properties (for example, absorptivity, nonporosity nature, intensity) of polymer composite which usually has a nonporous double continuation structure substantially, about 100 - about 100,000 -- desirable -- about 100 - about 60,000 -- and it has about 100 - about 5000 number average molecular weight most preferably.

[0037]I.b.ii. a polar monomer of the first type of an ethylene system unsaturation polar monomer of the radical (**) polymerization nature of oil insolubility is an ethylene system unsaturation polar monomer of water-soluble radical (**) polymerization nature which is insolubility substantially in an oil phase substantially. Both "it being oil insolubility (it is insolubility in an oil phase) substantially"

and "water solubility." It means that a monomer has less than about 0.5weight % of solubility in an oil phase, and a partition ratio in a predetermined temperature (preferably about 25 ** - 35 **) of concentration in an oil phase to concentration in aqueous phase shows less than about 0.005. Such a monomer may be nonionic, for example, acrylamide, or may be ionicity. A mixture of non-ion and an ionicity monomer may be used. An ionicity monomer which suits these standards, Although not necessarily restricted, sodium styrenesulfonate, acrylic acid potassium, Sodium acrylate, sodium methacrylate, acrylic acid ammonium, Sodium 2-acrylamide 2-methylpropanesulfonate, 4,4,9-trimethyl 4-azonia 7-oxa ****- 9-***** 1-sulfonate, A N,N-dimethyl- N-(beta-metacryloxy ethyl) ammonium propionate betaine, What was chosen from a group which comprises ethylene system unsaturated monomers of other dipolar ion nature which has trimethylamine methacrylamide, 1,1-dimethyl- 1-(2,3-dihydroxypropyl) amine methacrylamide, and the required requirements for solubility, those mixtures, etc. is included. A desirable polar monomer of oil insolubility from a Reason of the ease of combination, and the physical properties of a request when it polymerizes. What was chosen from a group which comprises acrylamide, sodium styrenesulfonate, sodium acrylate, 2-acrylamido-2-methyl-propane-sulfonic-acid sodium, sodium methacrylate, and those mixtures is included.

[0038]I. Many polar monomers known by this ethylene system unsaturation polar monomer industry of radical (**) polymerization nature other than b.iiil.b.ii show a certain amount of solubility to both water and an oil. They have about 0.5% or more of solubility in an oil phase, and a partition ratio in a predetermined temperature (preferably about 25 ** - 30 **) of concentration in an oil phase to concentration in aqueous phase shows about 0.005 or more. A radical (**) polymerization nature monomer of a useful polar ethylene system unsaturation which can be distributed between an oil phase of microemulsion of this invention and aqueous phase, Although not necessarily restricted, N-vinyl pyrrolidone, N-vinylcaprolactam, (METO) Acrylic acid, hydroxyethyl (METO) acrylate, itaconic acid, What was chosen from a group which comprises styrene-sulfonic-acid, N-substitution acrylamide, N,N-2 substitution acrylamide, N, and N-dimethylaminoethyl methacrylate, 2-acrylamido-2-methyl propane sulfonic acid, and those mixtures is included. A monomer in which desirable polar distribution is possible Acrylic acid (METO), N-vinyl pyrrolidone, What was chosen from a group which comprises N-vinylcaprolactam, N, and N-dimethylaminoethyl methacrylate, N,N-dimethylacrylamide, styrene sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, and those mixtures is included. A monomer in which the most desirable polar distribution is possible from a Reason of desirable character like physical strength which they can give to polymer composite. What was chosen from a group which comprises acrylic acid, N-vinyl pyrrolidone, N-vinylcaprolactam, N,N-dimethylacrylamide, and those mixtures is included.

[0039]I.c. water-soluble initiator aqueous phase may contain further a water-soluble radical polymerization initiator chosen from a group which comprises a mixture of a photoinitiator, and a photoinitiator and a thermal initiator if needed.

I.c.i. a water-soluble photoinitiator useful to water-soluble photoinitiator this invention -- a radiant ray (usually) When exposed to ultraviolet rays, it is a photoinitiator which generates a free radical, and it acts as an initiator for a polymerization (**) of the following polymerizable surfactant (**), a hydrophilic monomer, an oleophilic monomer, polymerization (**) nature oligomer, and when it exists. Benzophenone replaced by an ion portion, a hydrophilic portion, or its both although a useful water-soluble photoinitiator was not restricted; An ion portion, A thioxan ton replaced by a hydrophilic portion or its both and 4-substituent contain what was chosen from a group which comprises 4-substitution-(2-hydroxy-2-propyl) phenyl ketone which is ion or a hydrophilic portion. Although such ion or a hydrophilic portion is not necessarily restricted, it contains a portion chosen from a group which comprises hydroxyl, a carboxyl group, and a basis of carboxylate. Although water-soluble useful benzophenone is not necessarily restricted, it contains what was chosen from a group which comprises a 4-trimethyl aminomethyl benzophenone hydrochloride and benzophenone 4-sodium methanesulfonate. Although a water-soluble useful thioxan ton is not necessarily restricted, 3-(2-

hydroxy-3-trimethyl aminopropoxy) thioxan ton hydrochloride, What was chosen from a group which comprises 3-(3-trimethyl aminopropoxy) thioxan ton hydrochloride, thioxan ton 3-(2-ethoxysulfonic acid) sodium salt, and thioxan ton 3-(3-propoxysulfonic acid) sodium salt is included. Although water-soluble useful phenyl ketone is not necessarily restricted, ketone (4(2-hydroxy-2-propyl)-diethylene-glycol phenyl), (2-hydroxy-2-propyl) What was chosen from ketone and a group which comprises those water soluble salt is included (phenyl-4-butane carboxylate). A desirable water-soluble photoinitiator is a 4-trimethyl aminomethyl benzophenone hydrochloride.

[0040]the aqueous phase — a standard [weight sections / all the (**) / in microemulsion / heavy affinity kind 100] — about 0.05- about 1 weight section, preferably, the photoinitiator of about 0.1 - about 1 weight section is included, when used.

I.c.ii. a water-soluble thermal initiator useful to water-soluble arbitrary thermal initiator this inventions, When it exists (**) and is exposed [a hydrophilic monomer, an oleophilic monomer, polymerization (**) nature oligomer, and] to the heat which starts the polymerization (**) of a polymerizable surfactant, it is an initiator which generates a free radical, and it indicates in detail to the following. These thermal initiators are used only as assistance of a photoinitiator, when the perfect polymerization of a monomer has concern. Although a water-soluble suitable thermal initiator is not necessarily restricted, potassium persulfate, Ammonium persulfate, sodium persulfate, and those mixtures; A oxidation reduction initiator, For example, resultant; and 4,4'-azobis (the soluble salts 4-cyanopentanone acid and its) of a reducing agent which is chosen from the group which comprises the sodium metabisulfite and sodium bisulfite, and the above-mentioned persulfate What was chosen from the group which comprises (for example, sodium salt and potassium salt) is included. A water-soluble desirable thermal initiator is ammonium persulfate. Preferably, almost all the water-soluble thermal initiator is used at the temperature of about 50 ** - about 70 **, and, on the other hand, a oxidation reduction type initiator is used at the temperature of about 30 ** - about 50 **, the time of being used — a water-soluble thermal initiator — a standard [weight section / in microemulsion / heavy (**) affinity kind 100] — about 0.05- about 0.1 - about 1 weight section are included preferably about 1 weight section.

[0041]I.d. water-soluble additive agent aqueous phase may contain water-soluble various additive agents further if needed, in order to manufacture polymer composite which has specific character and/or appearance. Each additive agent is chosen so that a desired final product may be manufactured. For example, supposing a conductive polymer is desired, an electrolyte will be added and it will get. Supposing coloring polymer is desired, a color will be added and it will get. Although an example of a useful additive agent is not necessarily restricted, a water-soluble cross linking agent. What was chosen from (for example, methylenebis acrylamide), a pH adjuster, an electrolyte, a color, paints, a compound [activity / in drugs], and a group that comprises an activity compound, an auxiliary solvent, non-copolymeric polarity oligomer, those mixtures, etc. physiologically is included. Although not necessarily restricted, when it was desirable for polymer composite to be conductivity as for especially an electrolyte containing what chosen from a group which comprises potassium chloride, a lithium chloride, sodium chloride, and those mixtures, a useful thing became clear with various compounds of this invention. On the basis of all the 100 weight sections of aqueous phase, an electrolyte to about 5 weight sections may be contained at the maximum, and about 0.5 weight sections - about 3 weight sections are contained preferably.

[0042]Although non-copolymeric polar oligomer useful as an additive agent is not necessarily restricted, it contains what was chosen from a group which comprises poly(N-vinylpyrrolidone), a polyethylene glycol, poly(oxyethylene) alcohol, poly (ethyleneimine), and those mixtures. Such oligomer is added so that the bulk properties of obtained polymer composite may be affected, for example, so that hydrophilic nature may be given to this material. Fatty alcohol which has about 1 - a carbon atom of eight abbreviation although the usual auxiliary solvent is not necessarily restricted. (for example, glycerin) and polyether (for example, butyl cellosolve (trademark)). It is butylcarbitol (trademark), hexyl cellosolve (trademark), and hexylcarbitol (trademark), and what was chosen from

marketing and a group which comprises those mixtures is altogether included from Union Carbide. [0043] The thing which is added to the aqueous phase and which show solubility with all the water-soluble organic additive agents specific in the organic phase of microemulsion intrinsically will be understood easily. Each additive agent has the original partition ratio between the aqueous phase and an organic phase. For this reason, as long as there are no directions in particular, the above-mentioned constituent of the aqueous phase exists also in an organic phase, and will affect that character. It is unnecessary to an understanding and implementation of this invention, and to change a fixed quantity of all the specific partition ratios. [the additive agent indicated so far]

II. An oil phase term "organic phase", a "oil phase", and a "lipophilic phase" are used for a mutual compatible target in this Description. Before a polymerization start, the oil phase of microemulsion contains a reactant oleophilic additive agent a hydrophobic radical (**) polymerization nature monomer, a radical (**) polymerization nature polar monomer, an oil-soluble initiator, and if needed.

[0044] II.a. in the lipophilic phase of the microemulsion of hydrophobic radical (**) polymerization nature monomer this invention, the useful ethylene system unsaturated monomer of hydrophobic radical polymerization nature, Although not necessarily restricted, what was chosen from the group which comprises the ester derived from about C_1 of acrylic acid or methacrylic acid - abbreviation

C_{18} alkyl ester, i.e., acrylic acid, or methacrylic acid, and about C_1 - abbreviation C_{18} alcohol is included. Desirable acrylic (METO) acrylate Isononyl acrylate, What was chosen from the group which comprises isooctyl acrylate, 2-ethylhexyl acrylate, ethyl acrylate, n-butyl acrylate, decyl acrylate, dodecylacrylate, isobornyl acrylate, methyl methacrylate, and those mixtures is included. The most desirable alkyl acrylate monomer is chosen from the group which comprises ethyl acrylate, n-butyl acrylate, isooctyl acrylate, isobornyl acrylate, methyl methacrylate, and those mixtures.

[0045] An organic phase contains further the above-mentioned alkyl acrylate monomer and copolymerizable radical polymerization nature ethylene system unsaturation comonomer if needed, in order to change the glass transition temperature (T_g) of the polymer composite obtained. Desirable comonomer Styrene, acrylonitrile, and vinyl ester. Comonomer is chosen by the character of a request of double continuation polymer of the last solid including what was chosen from the group which comprises (for example, vinyl acetate, vinyl propionate, vinyl neo pentanoate, etc.). The double continuation microemulsion of this invention and in order to give the sufficient intensity and cohesiveness for the polymer composite produced by being manufactured, the gross weight standard of microemulsion — about 15- about 85 weight % — desirable — about 25- about 75 weight % — and — most — desirable — about 30- about 65weight % of a hydrophobic monomer is included. The presentation percent of each constituent in microemulsion will be determined by the person skilled in the art on the basis of the character of a request of a copolymer, as stated above. It explains further what selection of the ratio of a constituent is made, and the following embodiments and drawing 1 - the phase diagram of three illustrate it.

[0046] II.b. a radical (**) polymerization nature polar monomer — as mentioned above, in order that an organic substance may distribute between the organic phase/ aqueous phase of microemulsion, the organic phase of microemulsion, Probably, a part of radical polymerization nature polar monomer indicated by above-mentioned I.b.ii. and I.b.iii. is included when used. Each monomer indicated in it shows the original partition ratio, and the listing is not required because of an understanding of this invention, and implementation.

II.c. an oil-soluble initiator oil phase contains an oil-soluble radical photopolymerization initiator (photoinitiator), and contains a thermal initiator further if needed.

[0047] II.c.i. oil-soluble photoinitiator this invention — a useful oil-soluble photoinitiator — a radiant ray (usually) When exposed to ultraviolet rays, a free radical is generated, and it acts as an initiator for the polymerization (**) of a polymerizable surfactant, a hydrophilic monomer and/or oligomer, an oleophilic monomer, and when it exists (**). Although a useful photoinitiator is not necessarily restricted, it is a mixture of one Michler's ketone and benzyl, or benzophenone, What was chosen as

2 US,4,289,844,B which is about 1:4 weight ratio preferably from the photoinitiator system of the coumarin base of a description and the group which comprises preferably the system which uses 3 dimethoxyphenylacetophenone and/or a diethoxyacetophenone as a base is included. An oil-soluble photoinitiator is contained in microemulsion as a part of organic phase at first. The free radical by which it was generated at the time of an exposure performs the polymerization (**) of a monomer, and (**) the polymerization (**) of a polymerizable surfactant by both water and an organic phase. An organic phase contains about 0.01 - the oil-soluble photoinitiator of about 5 weight sections on the basis of all the (**) heavy affinity kind 100 weight section of microemulsion.

[0048]II.c.ii. in manufacture of double continuation polymer of this invention, arbitrary oil-soluble thermal initiator oil-soluble thermal initiators may be used for the above after a photopolymerization process like a description if needed, in order to complete a polymerization reaction. An oil-soluble thermal initiator useful to this invention is an initiator which generates a free radical, when exposed to heat, and it starts a polymerization (**) of a polymerizable surfactant, a hydrophilic monomer, oligomer, an oleophilic monomer, and when it exists, and it explains it to the following in detail. Although a suitable oil-soluble thermal initiator is not necessarily restricted, An azo compound like Vazo 64 (trademark) (2,2'-azobis (isobutyronitrile)) and Vazo 52 (trademark) (2,2'-azobis (2,4-dimethylpentanenitril)) (both are available from duPont); Benzoyl peroxide. And what is chosen from a group which comprises peroxides like lauroyl peroxide and those mixtures is included. A desirable oil-soluble thermal initiator is 2,2'-azobis (isobutyronitrile).

[0049]an organic phase — a standard [weight section / of a polymerization (**) nature compound in microemulsion / gross weight 100] — about 0 - about 5 weight sections — usually — being alike — about 0.05- about 5 weight sections, preferably, about 0.1 - an oil-soluble thermal initiator of about 5 weight sections are included, supposing it is used.

II.d. arbitrary reactant oleophilic additive agent organic phases may contain further one or more sorts of further radical reactivity constituents if needed, and although they are not necessarily restricted, they contain what was chosen from the group which comprises an oil-soluble cross linking agent, chain transfer agents, and those mixtures. Although the example of a useful cross linking agent is not necessarily restricted, divinylbenzene; 1,4-butanediol diacrylate, What was chosen from the group which comprises abbreviation C₄-abbreviation C₈ alkyl diacrylate; which is chosen from the group which comprises 1,6-hexanediol diacrylate, 1, and 8-octanediol diacrylate, and those mixtures is included. A desirable cross linking agent is 1,6-hexanediol diacrylate. Supposing a cross linking agent is added, it will change, the last physical properties, for example, condensation intensity, of polymer. An organic phase is further included if needed, supposing it uses about 0.1 - the cross linking agent of 75 weight % of abbreviation for about 0 - about 75 weight sections or more than it, and usual on the basis of all the oil phase 100 weight section. The quantity of the cross linking agent used determines the physical properties of polymer, for example, the insolubility to the inside of a solvent, an elastic modulus, and internal strength. In such a use, an organic phase usually contains the cross linking agent of about 5 - about 75 weight sections on the basis of oil phase 100 weight section. In order that a person skilled in the art may acquire desired physical properties, the quantity of a suitable cross linking agent can be determined, and he will understand that there is no maximum on actual of the cross linking agent by which such a person skilled in the art is used in the compound of this invention and in which it deals.

[0050]An organic phase contains a chain transfer agent further if needed. Although an example of a useful chain transfer agent is not necessarily restricted, it contains what was chosen from a group which comprises carbon tetrabromide, alcohol, mercaptan, and those mixtures. When it exists, a desirable chain transfer agent is isooctylthioglycolate. supposing an oil phase is used — a standard [weight sections / all the / oil phase 100] — the maximum — a chain transfer agent to about 0.5 weight sections — usually — being alike — about 0.01- a chain transfer agent of about 0.05 - about 0.2 weight sections may be included further preferably about 0.5 weight sections.

II.e. arbitrary refractoriness oleophilic additive agent oil phases contain further one or more sorts of

refractoriness oil-soluble additive agents if needed. Various refractoriness oil-soluble additive agents may be contained in microemulsion. Such materials are added so that it may have last physical properties or appearance with a specific polymer system and may be manufactured. Although an example of such arbitrary oleophilic additive agents is not necessarily restricted, it contains what was chosen as this industry from a group which comprises a plasticizer like one sort of phthalic ester known well. supposing an oil phase is used — a standard [weight section / oil phase 100] — about 0 — about 20 weight sections — usually — being alike — about 5 — a plasticizer of about 8 — about 15 weight sections is included preferably about 20 weight sections. [0051] In order to prepare surface-active agent microemulsion, it argues about the non-ion and ion (anion and cation) surface-active agent which are used for this invention below. A surface-active agent may be [which exist in microemulsion / the monomer and copolymeric], or may be non-copolymeric. As for a surface-active agent, it is preferred that it is copolymeric so that the polymer composite obtained may seldom become hypersensitivity in water. When the tolerance to water is unnecessary, a non-copolymeric surface-active agent is preferred from the Reason for the cost low generally.

1. A nonionic surface active agent nonionic surface active agent is usually a condensation product of the alkylene oxide which is organic aliphatic series or an alkyl aromatic hydrophobic compound, and hydrophilic nature, for example, ethylene oxide. it has the carboxy, hydroxy **, amide, or amino group in which the free water matter exists — all hydrophobic compounds are almost condensed with ethylene oxide, and a nonionic surface active agent can be formed. It is adjusted and deals in the length of the ethylene oxide chains of a condensation product so that desired hydrophobicity and the balance (hydrophilic-hydrophobic balance, i.e., HLB) of a hydrophilic component may be attained. HLB of a surface-active agent — the size of the hydrophilic nature (***** or polarity) of a surface-active agent, and a hydrophobic (***** or nonpolarity) basis, and the balance of strength — expressing . HLB of a nonionic surface active agent useful to this invention in order to prepare microemulsion — about 6 — about 19 — desirable — about 9 — about 18 — and it is about 10 — about 16 most preferably. A useful nonionic surface active agent contains what was chosen from the group which comprises the copolymeric nonionic surface active agents and those mixtures of the nonionic surface active agent of un-(**) polymerizing nature, and an ethylene system unsaturation.

[0052] 1.a. A non-copolymeric nonionic surface active agent, especially a nonionic surface active agent of useful refractoriness. So that HLB specified above may be attained, although not necessarily restricted. Fatty alcohol containing high-class fatty alcohol of straight chain shape or the shape of a branched chain -, for example, about 8, and a carbon atom of 20 abbreviation, and about 3 - 100 mol of abbreviation. What is chosen from a group which comprises preferably a condensation product of about 5 - 40 mol of abbreviation which about 5 - ethylene oxide of 20 mol of abbreviation condensed most preferably is included. Examples of an ethoxylation fatty alcohol surface-active agent of such non-ion are Tergitol(trademark)15-S series of Union Carbide, and a Brij (trademark) surface-active agent of ICI. A Tergitol(trademark)15-S surface-active agent contains C₁₁-C₁₅ secondary-alcohol polyethylene glycol ether. Brij(trademark)58 surface-active agent is polyoxyethylene (20) Sept Iles ether, and Brij(trademark)76 surface-active agent is polyoxyethylene (10) stearyl ether. Other suitable refractoriness nonionic surface active agents so that HLB specified above may be attained, although not necessarily restricted, 1 mol of alkylphenol containing about 6-12 carbon atoms of straight chain shape or the shape of a branched chain and a thing which was preferably chosen [about 5 - 40 mol of abbreviation] from a group which comprises about 5 - a polyethylene oxide condensate with 20 mol of abbreviation most preferably as for the ethylene oxide 3 [about] - 100 mol of abbreviation are included. An example of a refractory nonionic surface active agent is Igepal(trademark) CO and CA series of Rhone-Poulenc. An Igepal (trademark) CO surface-active agent contains nonylphenoxypoly(ethyleneoxy)ethanol. An Igepal (trademark) CA surface-active agent contains octylphenoxypoly(ethyleneoxy)ethanol.

[0053] Another group of an usable refractoriness nonionic surface active agent, Although not necessarily restricted, what was chosen from about 6 – about 19, and the group that comprises preferably the block copolymer of about 9 – about 18, the ethylene oxide that has about 10 – about 16 HLB value most preferably and propylene oxide, or butylene oxide is included. The examples of such a non-ion block copolymer surface-active agent are Pluronic (trademark) of BASF, and a surface-active agent of Tetronic (trademark) series. A Pluronic (trademark) surface-active agent contains ethylene oxide propylene oxide block copolymer. A Tetronic (trademark) surface-active agent contains ethylene oxide propylene oxide block copolymer, being the further — others — the refractoriness nonionic surface active agent satisfied, although not necessarily restricted — about 6 – about 19 — desirable — about 9 – about 18 — and it has about 10 – about 16 HLB most preferably. What was chosen from the group which comprises a sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, and polyoxyethylene stearate is included. The examples of such a fatty-acid-ester nonionic surface active agent are Span (trademark) of ICI, Tween (trademark), and a Myrj (trademark) surface-active agent. A Span (trademark) surface-active agent contains C_{12} - C_{18} sorbitan monoester. A Tween (trademark) surface-active agent contains poly (ethylene oxide) C_{12} - C_{18} sorbitan monoester. A Myrj (trademark) surface-active agent contains polyethylene oxide stearate.

[0054]

1.b. The suitable nonionic surface active agent for making it contain in the microemulsion of ethylene system unsaturation copolymeric nonionic surface active agent, this invention is an ethylene system unsaturation copolymeric nonionic surface active agent, Although not necessarily restricted, it is general formula $R-O-(R'O)_m-(EO)_{(n-1)}-CH_2CH_2OH$ (among a formula). R (about — about $[C_2-]$ — the C_{18} alkenyl, AKURIRIRU, and AKURIRIRU (about C_1 -about C_{10}) alkyl.)

Methacrylyl, methacrylyl (about C_1 -about C_{10}) alkyl, It is chosen from the group which comprises a vinylphenyl and vinylphenylene (about C_1 -about C_6) alkyl, and; R'O Two or more carbon atoms, It is chosen from the group which comprises the alkyleneoxy group of the bivalence derived from the epoxy compound which has three pieces or four carbon atoms preferably, For example, propylene oxide, It is chosen from the group which comprises those mixtures, such as butylene oxide, and; E is ethylene of bivalence, m expresses about 5 – about 100 integer, n expresses about 5 – about 100 integer, and the ratios of m to n are about 20:1 – abbreviation 1:20. What was chosen from the group which comprises an applicable thing is included. If the ratio of m and n is changed, HLB of a polymerizable surfactant will change. HLB required for the nonionic surface active agent of this invention is about 6 – about 19, and is about 9 – about 18 preferably, and is about 10 – about 16 most preferably. The example of such a copolymeric nonionic surface active agent is an alkylene polyalkoxyethanol surface-active agent, and is available at trade name Mazon BSN (trademark) 185 from PPG Industries, and 186 and 187. A Mazon BSN (trademark) surface-active agent contains alkylene polyalkoxyethanol.

[0055] 2. An anionic surface active agent anionic surface active agent, Usually, the hydrophobic part chosen from the group which comprises alkyl (about C_6 -about C_{20}), alkyl aryl, and an alkenyl group, And sulfate, sulfonate, phosphate, polyoxyethylene sulfate, The anion group chosen from the group which comprises polyoxyethylene sulfonate, polyoxyethylene phosphate and the alkaline metal salt of such an anion group, ammonium salt, and the third class amino salt is included. As a hydrophobic part. (About C_2 -about C_{18}) In this invention the specific ethylene system unsaturation copolymeric surface-active agent containing the anion group of alkenyl polyoxypropylene or (about C_2 -about C_{18}) alkenyl polyoxy butylene, and polyoxyethylene sulfate. It is useful although microemulsion is manufactured. The further useful anionic surface active agent is described below to this invention.

[0056] 2. the refractoriness anionic surface active agent which can be used in a refractoriness

anionic surface active agent this invention, Although not necessarily restricted, alkyl (about C_6 —about C_{20}), alkyl aryl sulfate, or sulfonate, For example, Sodium lauryl sulfate (as Polystep (trademark) B-3 from Stepan Co.) Marketing and sodium dodecylbenzenesulfonate (it markets as Siponate(trademark) DS-10 from Rhone-Poulenc); They are polyoxyethylene (about C_6 —about C_{20}) alkyl or alkylphenol ether sulfate, The ethylene oxide repeating unit in a surface-active agent is less than about 30 units, What is preferably less than about 20 units, and is most preferably less than about 15 units, For example, Polystep of marketing from StepanCo. (Trademark) B-1, Ailpal (trademark) EP110 of Rhone-Poulenc, and 115; They are the alkyl (about C_6 —about C_{20}) of phosphoric acid or alkyl phenoxy poly(ethyleneoxy) ethylmonoester, diester, and its salt, The ethylene oxide repeating unit in a surface-active agent contains what was chosen from the group which comprises the thing which is less than about 30 units, is preferably less than about 20 units, and is most preferably less than about 15 units, for example, Gafac(trademark) PE-510 of GAF, and Gafac(trademark) RE-610.

[0057]

2.b. A suitable anionic surface active agent for making it contain in microemulsion of ethylene system unsaturation copolymeric anionic surface active agent this invention is formula $R-O-(R'O)_m-(EO)_{n-1}-CH_2CH_2X$, although not necessarily restricted. the inside of [type, and R (about — about $[C_2]—C_{18}$ alkenyl —) [AKURIRIRU and] AKURIRIRU (about C_1 —about C_{10}) alkyl, methacrylyl, It is chosen from a group which comprises methacrylyl (about C_1 —about C_{10}) alkyl, a vinylphenyl, and vinylphenylene (about C_1 —about C_6) alkyl, and; R'O Two or more carbon atoms, An alkyleneoxy group of bivalence derived from an epoxy compound which has three pieces or four carbon atoms preferably, For example, it is chosen from a group which comprises mixtures of such an alkyleneoxy group, such as propylene oxide and butylene oxide, and; E is ethylene of bivalence, m expresses about 5 — about 100 integer; n expresses about 5 — about 100 integer, and ratios of m to n are about 20:1 — abbreviation 1:20. What was chosen from a group which comprises an ethylene system unsaturation copolymeric surface-active agent of] is included. If a ratio of m and n is changed, HLB of a polymerizable surfactant will change. HLB required for an anion copolymeric surface-active agent of this invention is about 3 — about 16 except for X-basis. X is the anion group chosen from a group which comprises alkaline metal salt, ammonium salt, or the third class amino salt of sulfonate, sulfate, phosphate, and such an anion group. An example of such a copolymeric anionic surface active agent is Mazon(trademark) SAM 211 of PPG Industries and Inc.

[0058]1. In cationic surface active agent this invention a useful cationic surface active agent, Although not necessarily restricted, what was chosen from a group which comprises quaternary ammonium salt in which a basis of a lower molecular weight of a basis of a higher molecular weight of at least one piece and two pieces, or three pieces combined with a common nitrogen atom, and formed a cation is included. Here, an anion made to balance electrically is chosen from a group which comprises halogenides (a bromide, a chloride, etc.), acetate, nit RITTO, and low-grade ARUKO sulfate (METOSURU Fet etc.), a substituent of the amount of polymers is often a higher alkyl group from that on nitrogen — about 10—, including about 20 carbon atoms, More, the substituent of low molecular weight can be low-grade alkyl, for example, methyl, or ethyl of a carbon atom of about 1 — four abbreviation, and it may be replaced by hydroxy **, for example depending on the case. One or more substituents may also contain an aryl portion, and it may be replaced by aryl, for example, benzyl, and a phenyl. about 1— it being low-grade alkyl, for example, methyl, or ethyl of about four carbon atoms, being replaced by low-grade polyalkoxy portion like a polyoxyethylene portion, and, including a hydroxy end group, A thing applicable to general formula- $R(CH_2CH_2O)_{(n-1)}CH_2CH_2OH$ ($-R$ is an alkyl group of bivalence of C_{1-4} combined with nitrogen among a formula, and n expresses about 1 — about 15 integer.) is contained in a possible low-molecular-weight substituent.

Independently, it is not combined with quaternary nitrogen through the above-mentioned low-grade alkyl, but 1 of such a low-grade polyalkoxy portion that has hydroxyl of an end, or two pieces may couple directly with quaternary nitrogen. An example of a quaternary ammonium halide surface-active agent useful to use by this invention, Although not necessarily restricted, it is methylbis(2-hydroxyethyl)****- ammonium chloride or oleyl ammonium chloride (respectively) from Akzo Chemical Inc. What was chosen from a group which comprises Ethoquad(trademark) C/12, O/12, and methylpolyoxyethylene (15) octadecyl ammonium chloride (Ethoquad(trademark) 18/25) is included.

[0059]The typical constituent concentration (weight %) in the microemulsion of this invention is as in the following table 1.

[0060]

[Table 1]

マイクロエマルジョン	有用	好適	最適
疎水性モノマー	15-85%	25-75%	30-65%
水	2-40%	5-50%	8-40%
極性種	2-60%	5-50%	8-40%
界面活性剤	5-70%	7-50%	9-35%

[0061]Each numerical value in Table 1 shows a rough value. These figures express weight % to the gross weight of microemulsion. The concentration of each ingredient is selected so that the whole may be 100%.

[0062]Since microemulsion forms spontaneously the manufacturing method of the microemulsion of manufacturing method this invention of microemulsion, without needing most intense stirring, it is comparatively easy. However, it is desirable to dissolve an oil-soluble photoinitiator in a hydrophobic monomer beforehand, and to dissolve beforehand all the water-soluble additive agents, an oil insolubility ionicity monomer, or a water-soluble photoinitiator in water, and to form a solution. Subsequently, the transparent and homogeneous microemulsion which does not carry out phase separation even if it mixes with a polar monomer, a surface-active agent, and other additive agents of all the and carries out aging of this hydrophobic monomer mixture and solution is manufactured. It is not necessary to use heat and almost all mixing processes are mostly carried out suitably at a room temperature (20-30 **).

[0063]The phase transition between the transparent microemulsion of a 1 phase system of this invention and the emulsion in which the two phase system became muddy is shown in drawing 1 - drawing 3. These are only illustration although these figures show the three phase figure about a hydrophilic pile affinity phase, a hydrophobic pile affinity phase, and the concentration of a surface-active agent (polymerization nature or non-polymerizable) about a certain specific microemulsion.

[0064]Drawing 1 is a phase diagram showing a microemulsion field transparent about the desirable constituent of this invention, and the emulsion field which became muddy. In this constituent, from PPG Industries, a surface-active agent is polymerization nature anionic surface active agent and Mazon (trademark) SAM211 marketed, and the heavy affinity phase of hydrophilic nature, It is a mixture which contains polyoxyethylene acrylate (PEOA), deionized water, and potassium chloride by the weight ratio 68:30:2, and a hydrophobic heavy affinity phase is a mixture which contains isobornyl acrylate and acrylic acid by the weight ratio 85:15. The slash field of drawing 1 shows the density range where the useful microemulsion by this invention was obtained.

[0065]Drawing 2 is a phase diagram showing a microemulsion field transparent about the desirable constituent of this invention, and the emulsion field which became muddy. The non-polymerizable nonionic surface active agent in which the surface-active agent is marketed from Union Carbide in this constituent, Are Tergitol15(trademark)-S-12 and the heavy affinity phase of hydrophilic nature,

It is a mixture which contains polyoxyethylene acrylate, deionized water, and potassium chloride by the weight ratio 68:30:2, and a hydrophobic heavy affinity phase is a mixture which contains isobornyl acrylate and acrylic acid by the weight ratio 85:15. The slash field of drawing 2 shows the density range where the useful microemulsion by this invention was obtained.

[0066]Drawing 3 is a phase diagram showing a microemulsion field transparent about the desirable constituent of this invention, and the emulsion field which became muddy. In this constituent, surface-active agents are a non-polymerizable cationic surface active agent, and Ethoquad (trademark) C/12, and the heavy affinity phase of hydrophilic nature. It is a mixture which contains polyoxyethylene acrylate, deionized water, and potassium chloride by the weight ratio 68:30:2, and a hydrophobic heavy affinity phase is a mixture which contains isobornyl acrylate and N-vinyl pyrrolidone by the weight ratio 85:15. The slash field of drawing 3 shows the density range where the useful microemulsion by this invention was obtained.

[0067]If microemulsion is obtained, a radical polymerization will be made to start and a polymerization will be made to cause by irradiating a person skilled in the art with an electromagnetism radiant ray by a well-known technique. After applying microemulsion on a flexible carrier web by one means of the daily use, such as roller coating, dip coating, knife coating, or extrusion coating. In an inert atmosphere (namely, atmosphere which does not contain oxygen), using a nitrogen atmosphere as everyone knows etc. polymerizes in the technical field concerned.

[0068]The plastic film which does not penetrate oxygen although ultraviolet rays are penetrated substantially, After combining microemulsion with the polyester film which has a silicone series remover on the surface which contacts microemulsion preferably, Microemulsion can also be polymerized in the air by using the fluorescence type ultraviolet ray lamp which emits the UV light of the wavelength range which the used photoinitiator absorbs, and irradiating with microemulsion through this film. Several kinds of lamps marketed can be used. A medium-voltage mercury-vapor lamp and a low-strength fluorescent lamp are in these, and it has various kinds of emission spectra, respectively, and the luminescence maximum is shown among 280-400 nm. It is preferred to use the fluorescence black light of marketing which has 90% of luminescence in the range which is 300-400 nm for convenience, and has the maximum in about 351 nm.

[0069]Generally, the total exposure dose should be made about $200\text{--}700\text{ mm J } [/\text{cm}]^2$. The maximum efficiency and speed of a polymerization are shown by the used expression of relations of the absorption feature of a photoactive compound, and the radiation property of an irradiation source. When the 2,2-dimethoxy-2-phenyl-acetophenone (known also as 2,2-dimethoxy-2-phenyl-1-phenylethanone and benzyl dimethyl ketal) which is a desirable photoinitiator is used, It is preferred that it is while not less than about 75% of radiant rays are 300-400 nm.

[0070]Although photopolymerization can also be carried out in an inert atmosphere, it can raise the admissibility for oxygen by making an oxidizability tin compound contain in a constituent as it writes in the US,4,303,485,B Description. As one of the photopolymerization method, after average light intensity irradiates microemulsion with the electromagnetism radiant ray of $0.01\text{--}20\text{ mW } [/\text{cm}]^2$ at about 280-500 nm first in wavelength, There is a way wavelength irradiates with the electromagnetism radiant ray whose average light intensity is higher than $20\text{ mW } [/\text{cm}]^2$ at about 280-500 nm.

[0071]Desirable photopolymerization method is sufficient method of carrying out a time exposure and giving about $680\text{ mm J } [/\text{cm}]^2$ about microemulsion in about 351-nm electromagnetism radiant ray. In this case, the photopolymerization time for about 10 minutes is required. Even if it gives continuously by the requirements for manufacture, the amount of ultraviolet energies which irradiates with this microemulsion is batch-like, and may be given. Microemulsion may be polymerized under ambient conditions. Ambient air temperature, ambient pressure, and ambient humidity are permissible.

[0072]If a polymerization is completed, superfluous moisture may be removed with the evaporation

method which uses a convection furnace and the source of infrared rays if needed.

The conductivity of polymer was measured by the measure resistance method of the four measuring method probe type of the examining method conductivity. Four metallic pins which kept the equal interval D (cm) were pressed against the polymer sample with the spring. The current of the intensity I (ampere) was sent through the outside pin. The amount V of voltage drops between inside probes (bolt) was measured. Resistivity is computed by a lower formula.

Resistivity (ωcm) = $2\pi DV/I$ conductivity is computed by a lower formula.

Conductivity = $1 / \text{resistivity}$ Reference documents : L. J. van der Pauw, Philips Res. Repts. 16 (1961) 187; J. Hornstra and L. J. van der Pauw, J. Electronics and Control 7 (1959) 169. [0073]The following cable addresses and trademarks are used on the cable address and the trademark book Descriptions.

Comp. ; comparative example DI water; — deionized water IBOA; — isobornyl acrylate IOA ;

Isooctyl acrylate MMA ; methyl methacrylate AA; — acrylic acid NVP ; N-vinyl pyrrolidone AcM ;

Acrylamide KAA. ; Acrylic acid potassium MazonTMSAM. 211 ;P PG. Alkylene polyalkoxy sulfate surface-active agent KCI made from Industries ; Potassium chloride PEOA; poly (ethylene oxide) acrylate or poly (oxyethylene) acrylate M.W.; [Molecular weight TergitolTM15-S-12;] Union.

Ethoxylated fatty alcohol surface-active agent TexaponTM L100 made from Carbide ; Sodium-lauryl-sulfate surface-active agent SiponateTMDS10 made from Henkel ; Dodecylbenzenesulfonic acid made from Rhone-Poulenc. The ammonium alkylphenol made from alkyl poly(ethyleneoxy) ethyl phosphate surface-active agent PolystepTMB-1;Stepan Chemical made from sodium surface-active agent GafacTMRE610;GAF. The ammonium alkylphenoxy poly(ethyleneoxy)ethanol sulfate surface-active agent made from ethoxy rate sulfate surface-active agent AlipalTMEP110;Rhone-Poulenc

[Translation done.]

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EXAMPLE

[Working example] Although the following embodiments explain this invention further, these embodiments do not limit this invention. Unless it refuses in particular, all of these embodiments and the part in the Description remainder, percent, a ratio, etc. are based on weight.

One to embodiment 6 Embodiments 1-6 carry out the microemulsion which has the aqueous phase (hydrophilic phase) and oil phase (canal phase) of the polymerization nature manufactured with polymerization nature and a non-polymerizable anionic surface active agent example 1.

[0075] The solution which contains 0.5 g of potassium chloride (KCl) in 7.5 g of deionized water in the jar of 1200 ml of embodiments was prepared at the room temperature. 9.4 g of acrylic acid (AA) and 22.2 g of poly (ethylene oxide) acrylate (PEOA) were added to this solution, and the hydrophilic phase was prepared. Subsequently, 48.0 g of isobornyl acrylate (IBOA) and MazonTM SAM 211 12.5-g surface-active agent were mixed to the hydrophilic phase, and transparent microemulsion was obtained.

The microemulsion of two to embodiment 6 Embodiments 2-6 was prepared like Embodiment 1 except for having used the ingredient and quantity which were displayed on the following table 2 instead of the ingredient and quantity which were indicated in the Embodiment 1.

[0076]

[Table 2]

実施例	重量 %					
	1	2	3	4	5	6
IBOA	48.0	35.5	33.4	32.9	32.5	31.8
AA	9.4	6.1	---	5.8	5.7	5.5
NVP	---	---	16.5	---	---	---
PEOA***	22.2	27.8	22.7	26.4	26.0	24.8
脱イオン水	7.4	12.2	10.0	11.6	11.4	10.9
KCl	0.5	---	0.7	0.8	0.7	---
Mazon TM SAM211*	12.5					
Texapon TM L100*		18.4				
Siponate TM DS10*			16.7			
Polystep TM B-1*				22.5		
Alipal TM BP110*					23.7	
Gafac TM RB610*						27.0

[0077]* All percents are based on the gross weight of microemulsion.

* Before using the anionic surface active agent of *PolystepTM B-1 and AlipalTMEP110 for preparation of microemulsion, it dried within a 105 °C furnace for about 10 to 15 hours, and it made activity 100%. The anionic surface active agent of MazonTMSAM 211, TexaponTM L100, SiponateTMDS10, and GafacTMRE610 was used as it was. MazonTMSAM 211 is a copolymeric anionic surface active agent. TexaponTM L100, SiponateTMDS10, PolystepTM B-1, AlipalTMEP110, and GafacTMRE610 are non-copolymeric anionic surface active agents.

* Number average molecular weight =750 of ** PEOA [0078]Seven to embodiment 14 Embodiments 7-14 illustrate the process of the microemulsion which has the aqueous phase (hydrophilic phase) and oil phase (canal phase) of the polymerization nature manufactured with the copolymeric and non-copolymeric nonionic surface active agent. These microemulsion was prepared like Embodiment 1 except for having used the ingredient and quantity which were displayed on the following table 3 instead of the ingredient and quantity which were indicated in the Embodiment 1.

[0079]

[Table 3]

実施例	重 量 %								
	7	8	9	10	11	12	13	14	
IBOA	47.1	46.1	47.4	42.6	44.8	39.4	44.1	47.4	
AA	9.3	9.0	9.2	8.3	8.7	7.7	8.6	9.2	
PEOA***	23.5	22.8	23.3	21.1	22.1	19.5	21.9	23.3	
脱イオン水	5.8	5.7	5.8	5.3	5.5	4.9	5.5	5.8	
KCl	0.5	0.5	---	0.5	0.5	0.4	0.5	0.5	
BSN™ 186*	13.8								
Igepal™ CA630*		15.9							
Tergitol™ 15-S-12*			14.3						
Pluronic™ L64*				22.2					
Tetronic™ 1304*					18.4				
Tween™ 20*						19.2			
Myrj™ 52*							19.2		
Brij™ 58*								13.8	

[0080]* All percents are based on the gross weight of microemulsion.

** BSNTM186 is a copolymeric nonionic surface active agent made from PPG Industries. It was then used (that is, it does not dry before use).

The remaining nonionic surface active agents of Table 3 are non-copolymeric nonionic surface active agents, and were used as it was also about these (that is, it does not dry before use).

* Number average molecular weight =750 of ** PEOA [0081]Embodiment 15 and 16 Embodiments 15 and 16 illustrate the process of the microemulsion which has the hydrophilic phase and canal phase of the polymerization nature manufactured with the non-copolymeric cationic surface active agent. Although these microemulsion was prepared like Embodiment 1, it used the ingredient and quantity which used N-vinyl pyrrolidone (NVP) instead of and were moreover displayed on the following table 4. [acrylic acid]

[0082]

[Table 4]

実施例	重量 % *	
	15	16
IBOA	31.3	35.6
NVP	8.0	7.1
PEOA***	14.7	31.3
脱イオン水	15.3	3.6
KCl	---	0.7
Rthoquad™ C/12*	30.7	
Rthoquad™ 18/25*		21.7

[0083]* All percents are based on the gross weight of microemulsion.

* * cationic surface active agent was used as it was (that is, it does not dry before use).

* Number average molecular weight =750 of ** PEOA [0084]The following Embodiments 17-25 explain the process of the polymer composite which has the double continuation structure by the polymerization of microemulsion.

The solution which contains 0.5-g KCl in 8.8 g of deionized water in the jar of 17200 ml of process embodiments of the polymer which has the double continuation structure by the polymerization of microemulsion was prepared at the room temperature. 9.4 g AA and 20.8-g PEOA were added to this solution, and the hydrophilic phase was made to form. Subsequently, 47.7 g IBOA,

Mazon™SAM211 12.5 g surface-active agent, and a 0.3-g benzyl dimethyl ketal photoinitiator were mixed to this hydrophilic phase, and transparent microemulsion was obtained to it. Then, this transparent microemulsion was poured in into the 5cmx15cmx2mm cell demarcated with the glass of the couple which has a release liner. Subsequently, the cell containing microemulsion was irradiated with the product [made by General Electric] F40BL type 40-W UV light which generates 1.9mJ from the place distant 6 cm for 20 minutes at the room temperature, and the polymerization was made to cause. After the polymerization, according to the four-point probe type measure resistance method, as shown in Table 5, the polymer solid showed conductivity, and it suggested that polymer composite had taken double continuation structure.

[0085]In Embodiments 18-24, the ingredient indicated to Table 5 in accordance with the above-mentioned method was mixed, and microemulsion was prepared, and solid polymer was prepared from the microemulsion. Polymer of hydrophilic nature, the adhesiveness by hydrophobic double continuation polymer composite, and non cohesiveness was manufactured by this method.

The comparative example 25 comparative example 25 illustrates the process of polymer which is not double continuation. Although the procedure of Embodiment 17 was adopted, however since deionized water was excluded, microemulsion was not formed. The obtained polymer was non-conducting intrinsically, as shown in Table 5.

[0086]

[Table 5]

実施例	重量 % *									比較例25
	17	18	19	20	21	22	23	24		
IBOA	47.7	56.1			22.5		48.3	48.8	47.7	
IOA			50.9	46.2	22.5					
NMA						45.2				
ベンジルジメチルケタール	0.3	0.5	0.5	0.5	0.3	0.8	0.5	0.5	0.3	
脱イオン水	8.8	6.0	10.0	7.7	8.5	8.5	11.3	9.5		
KCl	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5	
PEOA***	20.8	23.0		22.3	20.0	20.0			20.8	
AA	9.4		12.4		9.0	9.0		11.5	9.4	
NVP				7.8						
AcM								2.5		
KAA							13.3			
Mazon SAM™211	12.5	13.8	25.7	15.0	16.0	16.0	26.1	26.7	12.5	
*導電率×10 ⁻¹	22	170	263	197	12	5	10	112	0.06	

[0087]* All percents are based on the gross weight of microemulsion.

* Number average molecular weight =750 of $\omega^{-1}\text{cm}^{-1}$ *** PEOA [0088]The form of the polymer which might be followed by Embodiments 17 and 24 was observed by scanning electron microscope SEM (Bedford, goods Amray 1810 microscope marketed from Amray of MA.). Freeze fracturing of the sample is carried out in liquid nitrogen, And sputtering coating of the golden-palladium was carried out for 4 minutes at 10 kV using the sputtering system (Agawam, goods Ultra-Spec 90 LVC sputtering system marketed from Energy Beam Sciences of MA.). Magnification was made into 3000 or more times.

[0089]Drawing 4 shows the SEM microphotograph of polymer of Embodiment 17. Polymer of Embodiment 17 is flexible non cohesiveness polymer which has a nonporous form substantially. 0.1 micrometers or more in diameter a stoma or open space were not accepted at all, but polymer was nonporosity substantially. Drawing 5 shows the SEM microphotograph of polymer of Embodiment 24. Polymer of Embodiment 24 is non cohesiveness polymer without the pliability which has a nonporous form substantially. 0.1 micrometers or more in diameter a stoma or open space were not accepted at all, but polymer was nonporosity substantially.

[0090]Polymer of Embodiment 24 was prepared by the heat induction polymerizing method by the method indicated in the embodiment of the US,5,238,992,B Description (Outubuddin) for comparison. This polymer composite was non cohesiveness polymer without the pliability in which the big bubble was confined inside. It filled up, so that open space could not be permitted in this polymer, and it was not nonporosity substantially.

[0091]Although this invention was explained in connection with a special embodiment, please understand that it can change further. The Claims in this Description include such all transformation to be accepted if it is a person skilled in the art as it is chemically as equal as what was indicated here.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]A surface-active agent shows the phase diagram about the desirable microemulsion of this invention which is a copolymeric anionic surface active agent.

[Drawing 2]A surface-active agent shows the phase diagram about the desirable microemulsion of this invention which is a non-copolymeric nonionic surface active agent.

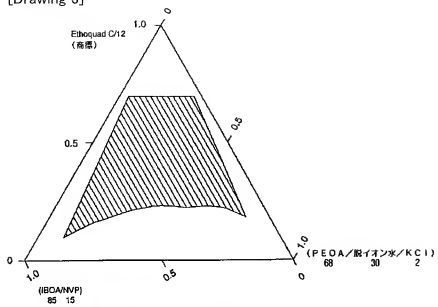
[Drawing 3]A surface-active agent shows the phase diagram about the desirable microemulsion of this invention which is a non-copolymeric cationic surface active agent.

[Drawing 4]It is a scanning electron microscope photograph which replaces the Drawings in which the organization of the polymer composite of this invention is shown.

[Drawing 5]It is a scanning electron microscope photograph which replaces the Drawings in which the organization of the polymer composite of this invention is shown.

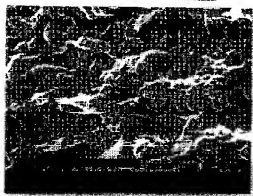
[Translation done.]

[Drawing 3]



[Drawing 4]

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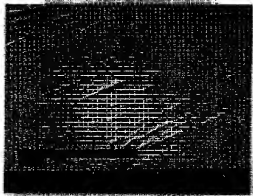


(写真)

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[Drawing 5]

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CORRECTION OR AMENDMENT

[Kind of official gazette]Printing of amendment by regulation of Patent Law Article 17 of 2
[Section Type] The 3rd Type of the part III gate
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[F]

C08F 2/48 MDJ
[Written Amendment]
[Filing date]Heisei 14(2002) January 21 (2002.1.21)
[Amendment 1]
[Document to be Amended]Description
[Item(s) to be Amended]Claims
[Method of Amendment]Change
[Proposed Amendment]
[Claim(s)]

[Claim 1]It is the polymer composite which has a nonporous double continuation structure substantially, including an optical start polymerization product of microemulsion which has aqueous phase and an oil phase, and said microemulsion is following (a) - (e). :

(a) 2 to 40 weight % of water;

(b) Following the (1) - (4),

(1) Radical polymerization nature or a copolymeric polar monomer of oil insolubility substantially;

(2) Radical polymerization nature or copolymeric polar oligomer of oil insolubility or water solubility, and oil solubility;

(3) Water-soluble and oil-soluble radical polymerization nature or a copolymeric monomer;

(4) 2 to 60 weight % of radical copolymeric ethylene system unsaturation polarity kinds chosen from a group which comprises mixture [of these]:

(c) 15 to 85 weight % of radical copolymeric ethylene system unsaturation hydrophobic monomers;

(d). Do not carry out copolymerization to a polar kind of (1) ingredient (b), and a monomer of an ingredient (c). A nonionic surface active agent, a cationic surface active agent, anionic surface active agents, and these mixtures, (2) An ethylene system unsaturation nonionic surface active agent which can carry out copolymerization to a polar kind of an ingredient (b), and a monomer of an

ingredient (c), a cationic surface active agent, anionic surface active agents and these mixtures, 5 to 70 weight % of surface-active agents chosen from a group which comprises both (3), (1), and (2); in a row

(e) 0.01 to oleophilic photoinitiator 5 weight section;

[However, weight % of the above (a), (b), (c), and (d), The amount of photoinitiators of (e) on the basis of gross weight of microemulsion, respectively The above (a), Said polymer composite in which it includes that it is based on gross weight of (b), (c), and (d)], and said optical start polymerization product has a nonporous double continuation structure substantially.

[Claim 2]Following (a) – (c) :

(a) (1) water;

(2) An ethylene system unsaturation polar monomer or oligomer of at least one sort of radical polymerization nature;

(3) Accept necessity and it is a water-soluble radical photopolymerization initiator.;

(4) Accept necessity and it is a water-soluble radical thermal polymerization initiator.;

(5) Accept necessity and it is a water-soluble additive.;

(6) refractoriness polarity oligomer; Reach if needed.

(7) Accept necessity and it is an auxiliary solvent.;

***** aqueous phase;

(b) A radical polymerization nature ethylene system unsaturated monomer of (1) hydrophobicity;

(2) Polymerization nature or a copolymeric polar kind;

(3) An oleophilic radical photopolymerization initiator;

(4) Accept necessity and it is an oleophilic radical thermal polymerization initiator.;

(5) Accept necessity and it is a cross linking agent.;

(6) Accept necessity and it is a chain transfer agent.;

(7) refractoriness polarity oligomer; Reach if needed.

(8) Accept necessity and it is an oil-soluble additive agent.;

A ***** organic phase; in a row

(c) A surface-active agent;

***** microemulsion.

[Claim 3]Following steps (a) – (c) :

(a) (1) water;

(2) An ethylene system unsaturation polar monomer or oligomer of at least one sort of radical polymerization nature;

(3) Accept necessity and it is a water-soluble radical photopolymerization initiator.;

(4) Accept necessity and it is a water-soluble radical thermal polymerization initiator.;

(5) Accept necessity and it is a water-soluble additive.;

(6) auxiliary-solvent; Reach if needed.

(7) Accept necessity and it is refractoriness polarity oligomer.;

A process of preparing the first mixture of ***** in an inert atmosphere;

(b) and (1) — at least 1 sort of hydrophobic radical polymerization nature ethylene system unsaturated monomer;

(2) A radical photopolymerization initiator;

(3) Accept necessity and it is a radical thermal polymerization initiator.;

(4) Accept necessity and it is a cross linking agent.;

(5) chain-transfer-agent; Reach if needed.

(6) Accept necessity and it is refractoriness polarity oligomer.

A process of preparing the second mixture of *****; in a row

(c) A process of mixing said first mixture into said second mixture in existence of a surface-active agent, and forming microemulsion under an inert atmosphere while stirring quietly;

A manufacturing method of ***** microemulsion.

[Translation done.]